# TREATISE ON
# QUALITATIVE CHEMICAL ANALYSIS

## SELLERS
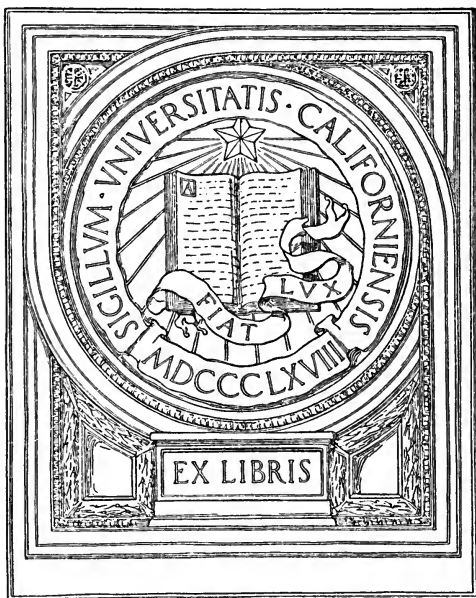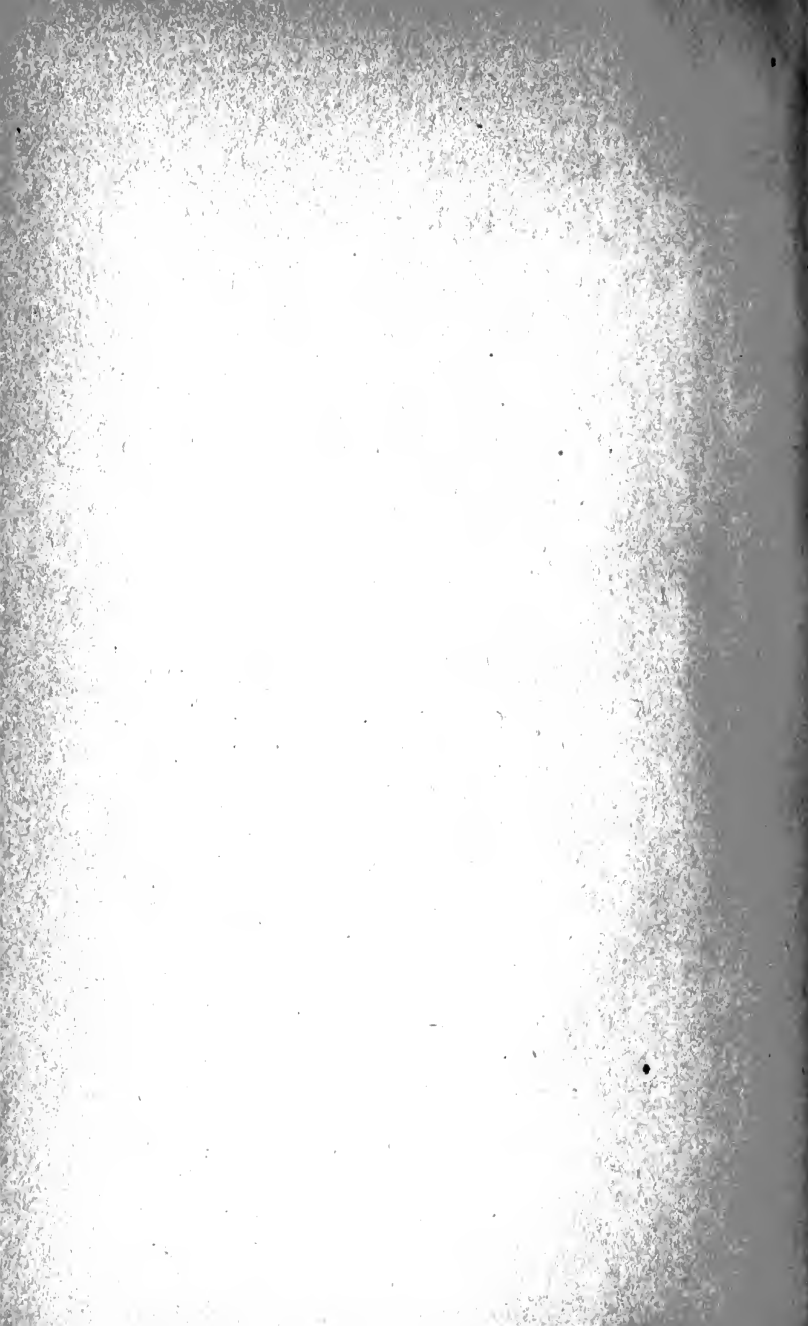
# AN ELEMENTARY TREATISE ON QUALITATIVE CHEMICAL ANALYSIS

BY

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# PREFACE

So many books on analytical chemistry are already in print that the question may be raised whether it is wise to add still another to their number; and therefore the author desires to present the following reasons which seem to him to justify the publication of the present work.

Most writers on analytical chemistry have gone either to the one or the other of two extremes. First, there are those who, like Fresenius or Prescott and Johnson, have endeavored to cover the entire field and to include the whole detail of analytical chemistry. Their works are indispensable to teachers and to students who make chemistry a specialty; but for beginners, who may not give more than one year of eight or ten hours a week to the subject, they are far too voluminous. On the other hand, there are those whose ardor for brevity has led them to the other extreme of condensing their material into "tables" and "schemes," — by which means they have magnified the empirical and have minimized the rational aspect of the subject, to its considerable detriment as a factor in liberal education.

In order to avoid either extreme the writer presents this elementary treatise having these features : —

1. A course short enough to be digested during the time allotted in an ordinary college curriculum, but at

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the same time intended to magnify the scientific and pedagogical nature of analytical chemistry.

2. A course both practical and progressive, — practical, in that the student can master the methods and principles of chemical analysis, and become a practical analyst; progressive, in that the chief aim of the book is to prepare the student thoroughly for advanced university work.

3. A course selected from the most recent and approved methods recorded in the best literature and verified by actual application in the author's laboratory. Among some of the improved methods are mentioned : —

(*a*) Reddrop's application of normal solutions to qualitative analysis. *Chemical News*, May, 1890.

(*b*) Hofmann's separation of arsenic, antimony, and tin, by modification of Marsh's test. Fresenius' *Qualitative Analysis*, 1897 edition, p. 299.

(*c*) Parr's separation of aluminum, chromium, and iron, by means of sodium peroxide. This method commends itself for its accuracy, its briefness and simplicity, and its certainty in detecting aluminum. Other methods depending on sodium hydroxide are defective, in that the reagent itself generally contains aluminum salts; sodium peroxide, by reason of its manufacture, does not contain perceptible traces of such salts. *Journ. Amer. Chem. Soc.*, 19, p. 341.

(*d*) Fresenius and Ruppert's separation of barium, strontium, and calcium, by means of the differences of solubility of their nitrates in ether-alcohol. Fres. *Qual. Anal.*, p. 160.

(*e*) Hager's separation of chlorine, bromine, and iodine, by means of the differences of solubility of their silver salts in ammonium " sesqui " carbonate. Fres. *Qual. Anal.*, p. 378.

4. A course free, as is thought wise, from the mechanical schemes in qualitative analysis. To this end, many of the usual tables of separation are omitted, and in their place some suggestive hints are given after the list of reactions for each group. Thus the student is expected and encouraged to exercise his judgment in selecting methods of analysis.

5. A course conformable to the modern dissociation theory of solutions. For example, why is the activity of certain acids modified by adding the salts of those acids ; or, more specifically, why is the solvent power of acetic acid decreased by adding some sodium acetate ?

6. A course giving more than ordinary emphasis to the spectroscope. Though spectroscopy is not *chemical* analysis, it possesses superior advantages over the chemical methods in these particulars : —

(*a*) Methods of greater exactness and readiness of execution.

(*b*) Methods superior for the preliminary detection of the alkali and alkali-earth metals. This is important, especially when the alkali-earth metals are combined with phosphoric, oxalic, and hydrofluoric acids.

(*c*) Methods superior for detecting certain metals, which, under some conditions, are evasive; *e.g.*, aluminum, manganese, and magnesium.

It is obvious that the study of the theory of solution and of spectroscopy may either be taken up in the order of the text or reserved for the last work in the course; and also that these subjects may be omitted entirely if a very elementary course is desired. In the latter case it would be possible also to omit the discussion of the

analysis for the metals of the third group in the presence of phosphoric acid, and those portions of Part II which are printed in small type.

The discussion of solutions in the brief space available in this book is necessarily much condensed, and possibly it is somewhat abstract and uninviting ; but in the author's opinion its introduction is desirable. Its purpose is to provide the student of qualitative analysis with the means for a rational interpretation of many apparently irrational reactions, and to help prepare him for the next stage of his chemical education, — namely, the study of quantitative analysis, — where the application of the laws of solutions is more abundant. No other text-book on qualitative analysis, within the author's knowledge, incorporates this dissociation theory of solution ; but its adaptability to qualitative instruction is shown by the fact that during the past half decade many teachers of the subject have devoted more or less time in their lectures to the practical application of the theory.

In the preparation of this book the following literature has been consulted : —

1. Many of the smaller text-books on qualitative analysis, including Noyes's, Newth's, and Volhard and Zimmermann's.

2. Standard works on general and analytical chemistry, including Watt's *Chemical Dictionary;* Roscoe and Schorlemmer's *Treatise on Chemistry ;* Mendeleeff's *Principles of Chemistry ;* Ostwald's and Nernst's works on physical chemistry ; Vogel's, Landaur's, and Roscoe's works on spectrum analysis ; Fresenius' works — the latest editions.

3. Memoirs in American and foreign chemical journals.

Grateful acknowledgment is made to Dr. R. W. Jones of the University of Mississippi, for his painstaking criticism of the manuscript of this little book. The author learned the chemical alphabet and received much inspiration and encouragement from this excellent teacher.

Appreciative mention also is made of the following gentlemen : Dr. H. C. White of the University of Georgia, for valuable suggestions as regards the adaptability of the book to elementary college work; Dr. J. W. Mallet of the University of Virginia, Dr. J. Stieglitz of the University of Chicago, and Dr. E. Renouf of Johns Hopkins University, for opinions concerning modern theories of solution; and Mr. H. V. Jackson of Mercer University, for general assistance.

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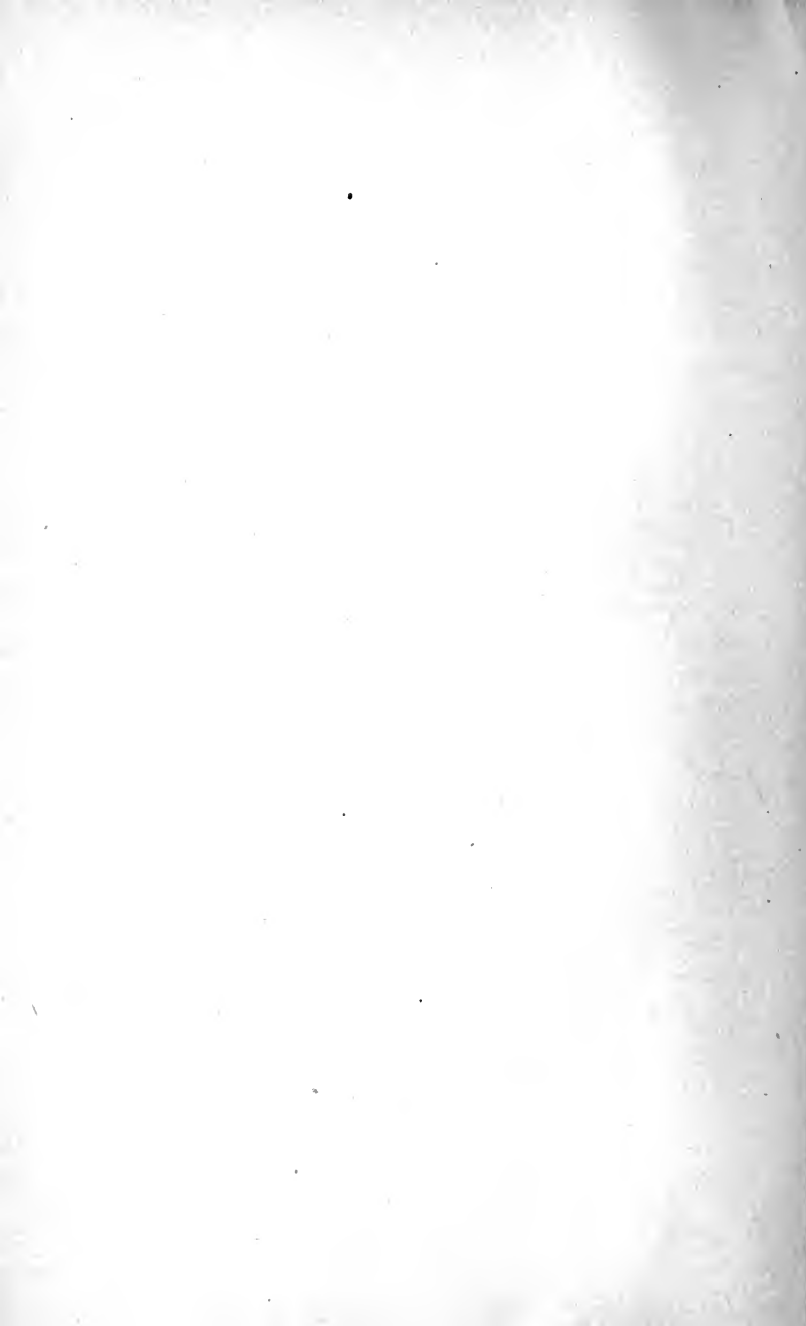
Macon, Ga., September, 1900

## PREFACE TO SECOND EDITION

The more important modifications made in this edition of the book are the appending of 13 pages of reference notes (see p. 163) and tables, revision of several of the processes of separation, and correction of a number of typographical errors.

For criticism and proof reading the author is indebted to many of his friends, among whom may be mentioned Professor W. H. Emerson and Dr. G. H. Boggs of the Georgia School of Technology, Dr. J. P. Montgomery of the Mississippi Agricultural and Mechanical College, Dr. Homer V. Black of the University of Georgia, Professor C. W. Steed of Mercer University, Professor G. P. Shingler of Emory College, and Professor Alexander Smith of the University of Chicago.

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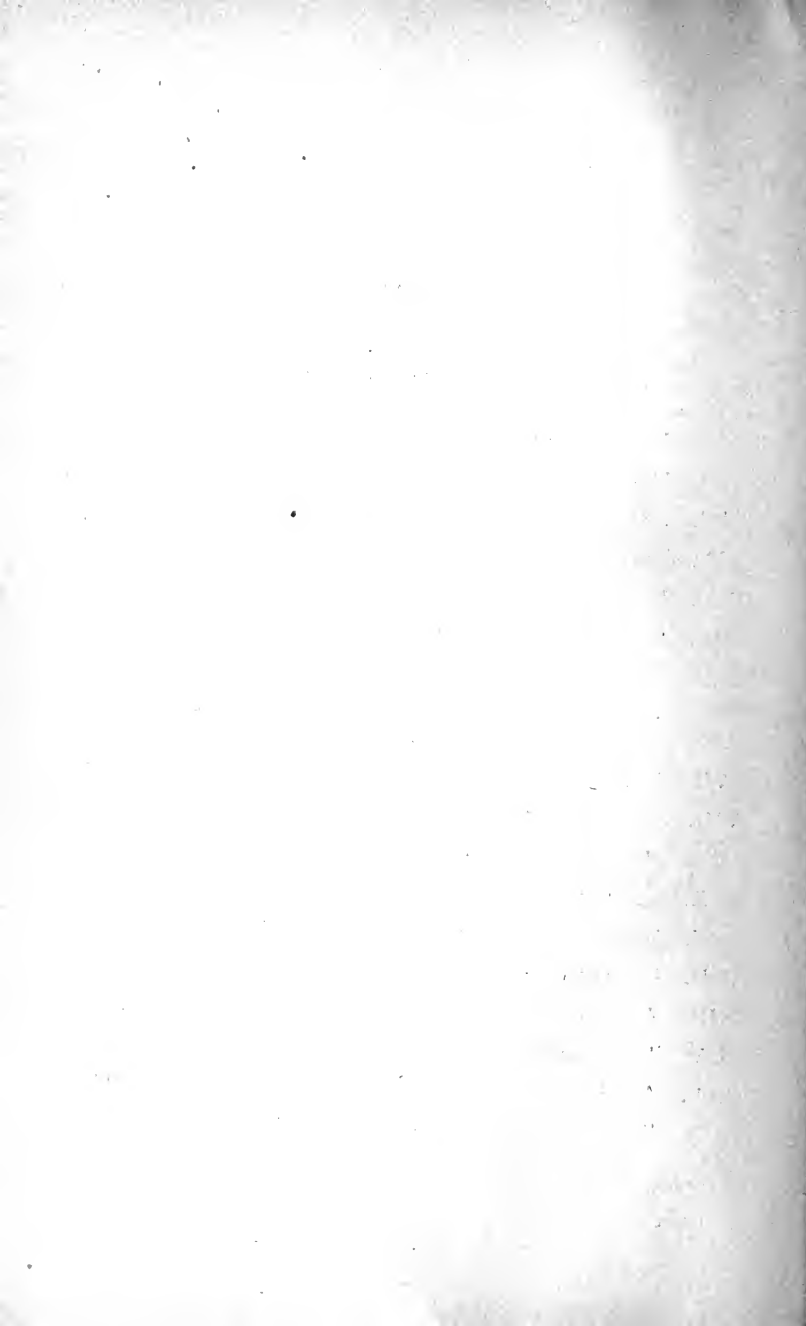
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# CHEMICAL ANALYSIS

## Part I — Analytical Operations

### CHAPTER I

#### INTRODUCTION

THE science of chemistry is commonly subdivided, for purposes of convenience in reference and teaching, into several tolerably distinct branches. The usual classification is into the main divisions of *inorganic* and *organic* chemistry, each of which may in turn be further divided into *descriptive*, *theoretical*, and *analytical* chemistry. Furthermore, analytical chemistry may itself be separated into the subdivisions of *qualitative* and *quantitative* analysis; the former having for its object the detection of chemical elements and compounds, and the latter the relative proportions of such substances. Analytical chemistry is commonly taught as a distinct branch, but it is not independent of the other divisions of the science; and hence, in all discussions in this book, both as to theory and manipulation, the presumption is that the student has, in the beginning of the course, a fair knowledge of the elements of general chemistry.

It obviously is essential to success in analysis that the analyst should have a clear idea of the operations

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involved in his work, as well as of the compounds with which he is dealing; and therefore, though both manipulation and theory are assumed to have been studied to some extent in connection with general chemistry, it is deemed well to review many of the ordinary operations from the analytical standpoint. The first part of this book is devoted largely to such a review; and it is earnestly recommended that it be studied closely, and that all of the experiments there given be carefully performed. It is true that the time spent on this preliminary work will delay somewhat the beginning of actual analysis; but it is believed that the student will be repaid in the end by the acquisition of a clearer conception of the work and of more skill in the manipulation of apparatus.

It should be remembered that it is far easier to form good habits than to correct bad ones; and so from the beginning the attention of the student should continually be directed to the importance of the following details which, though simple and apparently insignificant, are absolutely essential to continued success in analysis.

### CARE OF APPARATUS

(a) Keep all apparatus clean. This can best be done by cleaning the desk and apparatus before leaving for the day. Of course this does not apply to apparatus connected with unfinished experiments.

(b) When vessels containing materials of unfinished experiments are to be set aside, they should be properly labeled.

(*c*) Provide towels, clean rags, soap, and a covering for the clothes, either a long apron or a workingman's overalls.

(*d*) Have a place for all reagents and apparatus, and keep them in their place. Reagents for general use should not be kept at the individual desks. This is a source of great annoyance and injustice to one's neighbors.

(*e*) Use all care in keeping the reagents pure. Stoppers should not be placed on the desk while using the bottles, but held between the fingers. No foreign objects should be dipped into the bottles, nor should any excess of reagents be poured back into the bottles.

(*f*) Use small quantities of reagents. It is best to add liquid reagents, drop by drop, with frequent shaking of the test-tube, so that secondary reactions can be observed.

### LABORATORY NOTES

Provide a well-bound notebook for the subject and use it for nothing else. Keep accurate and methodical records of all experiments performed. These records should be made during or immediately following the performance of the experiment, and not transferred or erased afterwards. Original notes of an unsuccessful experiment are more valuable than a well-written description of a successful experiment, if the latter is composed in the absence of the experiment.

Some states prescribe by law that chemists, in giving expert testimony before the courts, shall present only

such data as are recorded in the presence of the experiments.

If desirable the original notes may be written on alternate lines or pages, and other notes of interpretation added at leisure. But the latter should be recorded with differently colored ink, or otherwise distinguished, in order that the original notes be not confused with subsequent additions.

# CHAPTER II

## THEORY OF ANALYTICAL OPERATIONS

**Nature of Analytical Chemistry.** — Analytical chemistry has already been defined as the art of recognizing the elements, or compounds, which may be present in any substance ; and, as the nature of the art implies, it commonly is practiced upon mixtures of one kind or another. Such mixtures may be mechanical only; and in such a case, if the elements of the mixture are sufficiently characterized by their color, crystalline form, or other external properties, it may be possible to identify or even to separate them by purely mechanical means. But the mixtures with which the chemist most commonly has to deal are those in which the strictly mechanical element plays a minor part. Such mixtures are produced when, by any appropriate means, two or more substances are brought into such intimate contact that they interpenetrate each other even to their minutest particles — the molecules. We have examples of mixtures of this class in the air, which practically is a homogeneous mixture of its constituent gases and vapors ; in common " solutions," such as are produced when any suitable material, like salt or sugar, is treated with some liquid which, like water, has the power of " dissolving " the material in. question ; or in alloys, which are produced when two or

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more metals are united by fusion into a mass which is, at all points, of uniform composition. Of these mixtures, the commonest are the solutions; and these are so important, from the standpoint of the analytical chemist, that it is desirable to spend some time in a careful study of their properties.

**Solution.** — In a general sense a solution is the product of the homogeneous absorption of a gas by a gas, or of a gas by a liquid, or of a liquid by a liquid, or of a solid by a liquid; and in recent years the term " solid solution " has been applied to certain homogeneous solid mixtures of which the alloy mentioned above may serve as the type. But specifically, in speaking of a solution, we have in mind the liquid product of the absorption by a liquid, called the *solvent*, of a gas, a liquid, or a solid, called the *solute*.

It has been found of all gases, and of some liquids, that they are capable of mixing homogeneously with one another in all proportions; but, on the contrary, it has not been found possible, under ordinary conditions, to dissolve a gas or a solid in a liquid in any desired proportion. Sooner or later a point is reached where the solvent refuses to take up more of the solute; and at this point the solution is said to be saturated. In most cases the application of heat to a saturated solution will enable it to absorb more of the solute; and the application of cold will usually result in the separation of a part of the material already dissolved. In such cases we may recover a portion of the solute by the mere chilling of its saturated solution; and in cases

where the solute is practically as soluble at low temperatures as at high ones, we may reach the same end by removing a part or the whole of the solvent by evaporation. It may be mentioned at this point that we have still another means of separating the solute from its solution; *viz.*, by the addition to the solution of some material which will decrease the solubility therein of the solute, without changing the identity of the latter. This process of separation is of considerable practical importance, and we shall presently have occasion to refer to it again.

### Experiment 1

(*a*) Dissolve 5 grams of potassium nitrate in 25 c.c. of distilled water, at a temperature of 15°–25° C. Then add successive portions of 1 gram each, shaking after each addition until all has dissolved that the solution will hold at this temperature. Note the total amount added and then raise the temperature of the solution to about 60°, — as hot as the hand can bear without too much discomfort, — and add more of the finely powdered salt while keeping the solution from cooling. Note the extra amount which is needed at this temperature to saturate the solution. Now cool the solution quickly and note the result. Compare any material which may separate with potassium nitrate.

(*b*) Dissolve 5 grams of common salt in 25 c.c. of distilled water at 15°–25°. Now add successive portions of $\frac{1}{2}$ gram, shaking after each addition until the solution is saturated. Note the total amount dissolved. Raise the temperature as in the preceding part of the experiment, and see whether it is possible to dissolve more salt in the hot solution. Allow any undissolved material to settle, and then pour off some of the clear solution into a clean dry test-tube, and cool as much as possible. Note the result. Evaporate a portion of this solution and compare the residue with salt.

(c) To about 25 c.c. of a clear saturated solution of common salt add 50 c.c. of concentrated hydrochloric acid, stirring all the time. Note the result, allowing the mixture to stand for some minutes. Pour off the clear liquid from any material which may have separated, and press a little of the latter between filter papers, to remove the acid liquor. It will be well to remove the last traces of acid by washing the residue with a little saturated brine. Compare the residue with common salt.

It will have been seen, in the performance of these experiments, that the recovered solute is of the same character as the original solute. But there are forms of solution in which this is not the case.

### Experiment 2

Dissolve a small piece of zinc in dilute hydrochloric acid and evaporate the solution to dryness. Compare the residue with metallic zinc.

Solution of this kind may be called *chemical* solution, in distinction from the *simple* solutions of Exp. 1. It will be seen that it involves

(1) a compound solvent — HCl + water — which itself is a simple solution; and a solute, Zn;

(2) a chemical reaction between the solute, Zn, and one constituent of the solvent, $HCl - Zn + 2\ HCl = ZnCl_2 + 2\ H$ — in which reaction the identities of the solvent and of the solute are changed;

(3) a simple solution, — $ZnCl_2$ + water.

Chemical solution is usually the result of the mutual reaction between

(1) an acid, or a base, and a metal;

(2) an acid, or a base, and a salt;

(3) an acid and a base.

But it may happen, as when metallic sodium is dissolved in water, that the phenomenon cannot be classified under any of these heads.

Simple solution is often a necessary predecessor of chemical solution, as has been seen in Exp. 2; and, in general, it prepares the way for chemical action by placing the reagents in close contact.

### Experiment 3

Mix .5 gram of dry potassium iodide with .5 gram of dry mercuric chloride in a dry mortar, and rub the mixed salts well together with the pestle. Note the result. Add a little water and rub again.

Furthermore, simple solution may be necessary to the continuance of chemical action, in order that the products of reaction may be removed from between the reagents.

### Experiment 4

Add a bit of zinc to 5 c.c. of concentrated sulphuric acid in a test-tube; leave for a few moments, noting all that happens. Now transfer the contents of the tube to a dish containing 15–20 c.c. of water.

When zinc is treated with concentrated sulphuric acid,[1] chemical action occurs for a short time only, and then ceases entirely. The explanation is probably this: zinc sulphate, insoluble in concentrated sulphuric acid, coats the zinc and prevents further contact of the reagents. The addition of water, in which zinc sulphate is very soluble, removes the coating and permits chemical action to go on once more.

**Properties of the Solute.**—So far in our study of the phenomena of solution, we have considered only those properties of the solute which are associated with its solid condition, — when, in point of fact, it cannot properly be called a solute. Let us now see whether we can discover anything concerning the properties of the true solute, — the body *in* solution.

We have seen that a solution which is saturated
with a given body at one temperature may acquire the
power of dissolving an additional quantity of that body
in consequence of an elevation of temperature, and
that, on the contrary, it may give up a portion of its
solute if its temperature is lowered.  That is to say,
if we have a "system" consisting of a limited quantity
of some saturated solution in contact with an excess of
its solute, there will be for any given temperature a
concentration of the solution at which there will be
a condition of equilibrium between the dissolved and
undissolved solute.  This condition is entirely analo-
gous to that which is observed when a volatile liquid
is exposed in contact with a limited volume of air or
other gas.  In the latter case the liquid will volatilize,
— rapidly at first, and afterwards more slowly, — until
the concentration of its vapor in the atmosphere to
which it is exposed has reached a certain limit which
will be dependent on the temperature.  With a rise in
temperature, more liquid will pass into the state of
vapor; with a fall, a portion of the liquid already
vaporized will be condensed again.

This analogy has been recognized for many years;
but it is now hardly more than a decade since first its
completeness was fully demonstrated.

**Colloids and Crystalloids.**[1] — It had been shown by
Graham (1842)[2] that certain *colloid* solutes, whose solu-
tions are not real liquids, but emulsions, cannot pass
through porous membranes [3] — such as parchment —
and that most *crystalloid* solutes, whose solutions are
real liquids, readily penetrate such septa.  He first

put separate solutions of a colloid and a crystalloid into separate open cylinders whose bottoms were closed with parchment, and then suspended the cylinders in vessels of water so that the membranes were immersed. After a few hours a large part of the crystalloid had passed through the parchment into the water in the outer vessel; and by renewing this water all of the crystalloid was finally extracted from the cylinder. From the other cylinder, however, no colloid had passed out.

**Osmosis.** — Pfeffer,[1] the botanist, in demonstrating and measuring the internal bursting force of plant cells (1877), established the fact that crystalloids, though they do not pass through the so-called " semi-permeable " membranes, — of which protoplasm [2] is a type, — do press strongly against the partition in their futile attempt to penetrate it. Connecting a mercury gauge and thermometer with a membrane, composed of a porous cell coated with copper ferrocyanide, and charging this apparatus with saccharine solutions of different strengths, he found that different concentrations of solution produced correspondingly different pressures within the apparatus when the temperature was kept constant, and that for any given concentration the pressure varied as the absolute temperature. He showed, therefore, that the relations of concentration, pressure, and temperature, which are shown by sugar in its solutions, are identical with those manifested by gases, — of which it will be remembered that the concentration or density of a given mass varies directly as the pressure and inversely as the absolute temperature. To the form

of tension exercised by the dissolved sugar he gave the name *osmotic pressure.*

**Law of Osmotic Pressure.** — Van't Hoff [1] (1887) found that a large number of solutions behave like that of sugar, and announced the following law: *The osmotic pressure of a substance in solution is identical with the pressure which it would exert were it in the form of a gas occupying the same volume* (*i.e.*, the volume of the solution) *at the same temperature.*[2]

We may conveniently express the simple law which governs the phenomena of gas and osmotic pressures in the following form: —

$$V = \frac{MT}{p} \qquad \text{or} \qquad p = \frac{MT}{V},$$

wherein $M$ represents the number of molecules [3] in a given body of gas, $T$ and $p$ the temperature and pressure, and $V$ the volume. Certain gases, such as oxygen, nitrogen, and hydrogen, are obedient to this law within very wide limits; but there are vapors whose behavior with regard to it is apparently anomalous. Evidently $V$ can be made constant, and $T$ and $p$ can be measured with any desired degree of accuracy. And therefore unless there can be a change in the value of $M$, any change in $T$ ought to be accompanied by an exactly proportional change in $p$. Now we find that certain vapors — such as that of ammonium chloride — give greater pressures than can be accounted for by either the value of $T$, or the value of $M$ which is based upon the commonly accepted molecular weight; and, as has been indicated, we find the explanation of this behavior in

the fact that the molecule $NH_4Cl$ is split up, or " dissociated," [1] when we seek to vaporize it, into the smaller molecules $NH_3$ and HCl. The analogies between the behavior of gases and substances in solution seem to extend to this phenomenon of dissociation, for it has been observed of many solutes that their osmotic pressures are so large as to be accounted for only on the supposition that their molecules are split up in solution and thereby increased in number. Sugar and other bodies of its neutral character obey the simple law as stated above; but acids, bases, and salts in aqueous solution usually exhibit anomalous pressures.

**Freezing Point Depression.**— Moreover, this is not the only evidence which bears upon the question of the dissociation of the molecules of solutes. It is a matter of common knowledge that the boiling and freezing points of aqueous solutions are respectively higher and lower than those of pure water. These relations were studied carefully by Raoult,[2] who showed that the phenomenon is a general one and that :—

(a) When any substances are dissolved in inactive solvents, the changes in the freezing and boiling points of the solvents vary with the amounts of substance dissolved.

(b) When equal weights of different substances are dissolved in equal amounts of the same solvent, the changes vary inversely with the molecular weights of the solutes.

It was found of many bodies — such as sugar — that equal depressions of the freezing point were produced by the solution of equimolecular proportions in

water; and in such cases the depressions were *exactly* in inverse ratio to the molecular weights. In other cases, however, the solutions of equimolecular weights of different substances produced unequal depressions; and the solution of different weights of a given substance produced depressions which were not in exact ratio to the weights so dissolved. In the latter anomalous cases the depressions were greater than seemed to be called for by the amount of matter which had been dissolved, as naturally would be the case if the molecules of the dissolved substances were dissociated into more numerous and smaller molecules; and the substances which exhibited this behavior were those which show abnormal osmotic pressures, namely, the majority of acids, bases, and salts.

In these two pieces of independent evidence we have a strong demonstration of the fact that many substances exhibit, when dissolved in water, a peculiar structural condition in which their molecules are split up into smaller bodies than are indicated by their accepted formulæ; and we have to inquire what further evidence we have which will throw light upon the precise nature of these submolecules. We shall find this evidence in connection with the behavior of solutions which are subjected to the passage of an electric current.

**Electrolytes.** — It has long been known that the conductivity exhibited by liquids is unlike that of metallic conductors, in that the latter are not affected chemically by the passage of a current, whereas the former are decomposed with separation at the electrodes —

the points where the current enters and leaves the liquid — of products of varying character. In 1834 Faraday[1] suggested, in explanation of this phenomenon, that the liquid which conducts electricity has in solution a compound whose molecules are divided into freely moving particles, some of which are charged with positive and the rest with negative electricity. He named such compounds *electrolytes;* and to the hypothetical fragments of their molecules he gave the name of *ions.* Those which were assumed to be positively charged were called *cations*, and were either metals, or atom-complexes, like $NH_4$, which react analogously to metals. Those bearing a negative charge were termed *anions*, and were such bodies as the halogens and acid radicles. The attraction or neutralizing effect which ions of opposite polarities were supposed to exercise upon each other, was held to maintain the identity of the solute until the solution was subjected to the passage of an electric current; whereupon the introduction of electrodes of opposite polarities upset the equilibrium previously existing between the ions and caused them to migrate, — the negative ions going toward the positive electrode, and the positive ions in the opposite direction. The appearance of decomposition products at the electrodes was explained as being due to the union of the ions, upon arrival at those points, to the molecular condition or to compounds with the elements of water.

In 1887 it was demonstrated by Arrhenius[2] that the solutions which exhibit normal osmotic pressures and freezing point depressions are nonconductors of elec-

tricity, and that their solutes are not electrolytes. Conversely, the solutions which give abnormal osmotic pressures were proved to contain ionized solutes; and it was shown, furthermore, by highly accurate experimental methods, that the degree of their conductivity is proportional to the amount of dissociation as measured by the osmotic pressure. Between the extremes presented by bodies like sugar, which are characterized by little chemical reactivity and the absence of conductivity and dissociation, and such substances as salts and strong acids and bases, which are distinguished by great reactivity and perfect conductivity and dissociation, were arranged the other varieties of chemical compounds, which possess various but proportional activities of the three kinds.

With the establishment of these facts the phenomenon of electrolytic dissociation received a new significance from the standpoint of analytical chemistry. The behavior of molecules in solution was seen to be chiefly dependent upon their tendency toward or from dissociation. The solutions of strongly ionized bodies are characterized rather by the reactions of the ions than by the properties of the undissociated molecules. In the case of sodium chloride, for example, the solution presents certain definite properties which are characteristic of the chlorine and sodium ions, and practically none which are characteristic of salt itself. In the case of sugar solutions, on the contrary, such properties as are manifested are those of the sugar molecule alone; and no indication is to be seen in them of the nature of the constituent elements of sugar.

**Analytical Significance of Ions.** — Borrowing an illustration from Ostwald, let us assume that we have to deal with 50 basic and 50 acidic units of some kind, which may in theory unite to form 2500 distinct compounds with as many sets of distinctly individual properties. Were the analyst compelled to recognize these compounds singly, in the solid condition, he obviously would have to be familiar with the properties of each individual among the whole number; and were he to attempt to identify the individuals that might be present in a mixture, the task would be beyond accomplishment. Were the compounds not dissociable in solution, his problem would still be scarcely less difficult of solution ; but, being dissociable, his task is made comparatively light. Since the properties of the solution of an ionized compound are merely the sum of the properties of its ions, and since the total number of ions with which we have assumed it necessary to deal is 100, it follows that the knowledge of 100 sets of properties is sufficient for the identification of any of the 2500 compounds. If, as it sometimes happens, the substance under examination is not soluble or readily dissociated, the analyst has only to convert it by appropriate means into a body which *is* soluble and dissociable, and then to determine its nature from the character of the latter substance.

**Laws of Electrolytic Dissociation.** — So far we have considered only the qualitative effects of electrolytic dissociation ; let us now examine briefly the quantitative effects, which are of no less importance to the analytical chemist.

As has been said already, different electrolytes have been found to show great dissimilarity in conductivity and ionization, even when dissolved in equimolecular proportions. But it also has been found that all are obedient to the same law with regard to the degrees of their dissociation, and that the dissimilarities are accounted for by constants which depend upon the nature of the electrolytes. The observed relations between the amounts of dissociated and undissociated electrolyte in a solution are expressed most simply for binary compounds in the equation

$$a.b = k.c,$$

wherein $a$ represents the concentration of the positive ions, $b$ that of the negative ions, $c$ that of the molecules of undissociated material, and $k$ a constant function of the electrolyte. By assuming a value, such as unity, for the total amount of electrolyte in solution, and by representing the amount of dissociated material by $\alpha$, and the volume of the solution by $v$, we may expand this equation to a somewhat more instructive form : —

$c$, concentration of undissociated electrolyte $= \dfrac{1 - \alpha}{v}$;

$a$ and $b$, concentrations of the two ions, — either ion $= \dfrac{\alpha}{v}.$

By substitution we obtain the equation in the form

$$\frac{\alpha^2}{1 - \alpha} = kv.$$

Inspection of these equations, which are merely the formal expression of observed fact, reveals : —

(1) that increase in $a$ (or $b$) will be accompanied by an increase in the ratio $\dfrac{a.b}{c}$, *i.e.*, the free ions will increase and the molecules will decrease;

(2) that decrease in $a$ (or $b$) will have the opposite effect, *i.e.*, the free ions will decrease and the molecules will increase;

(3) that the degree of dissociation may vary in either direction according as $k$ is increased or decreased by variation in the nature of the electrolyte;

(4) that dilution of a solution, and corresponding increase of $v$, will call for an increase in the *proportion* of dissociated solute, the degree of dissociation approaching totality as its limit, as the dilution is indefinitely increased;

(5) that concentration will have the opposite effect, and that the ratio of dissociated to undissociated solute will reach its minimum limit in a saturated solution.

Further inspection of the equation $a.b = k.c$ will reveal another fact which is of great practical significance for the analytical chemist. It is evident that in the solution of any given electrolyte, at a fixed temperature, the only possible variants will be $a$, $b$, and $c$. Let us suppose that it is possible in some way to introduce an added quantity of one ion, so that either concentration $a$ or $b$ will be increased. This being done, the increase in the product $a.b$ will demand an increase in the value $c$. But the only way in which $c$ may be increased is through the return from dissociation of a certain proportion of the ions. Assuming the concentration $b$ to have been increased, the concentration $a$

must be diminished until, by the decrease in $a.b$ and the corresponding increase in $c$, the original condition of equilibrium has been restored. In case that we are dealing with a saturated solution of the electrolyte, any increase in $c$ will result in supersaturation of the solution; and we shall see that a portion of the solute may separate in solid form. In fact, we have already seen this in a practical way in Exp. 1, $c$.

In the saturated sodium chloride solution of that experiment, a considerable portion of the solute was present in the form of Na and Cl ions; and the remainder was present in the molecular condition in quantity sufficient to produce saturation. The addition of concentrated HCl, whose solution is very strongly dissociated, introduced a very large excess of Cl ions in the salt solution; and, in consequence, the reunion of sodium and chlorine ions to the molecular state was set up and continued until equilibrium had been restored. But as the solution had already been saturated with the molecules of salt, these reformed molecules were forced to separate in the solid form.

If we dissolve together two substances which are dissociated more equally, such as KCl and NaCl, we find that less action of this sort takes place; but when, of our two solutes with a common ion, one is more strongly dissociated than the other, the weaker is forced back to the molecular and inactive condition.

The constant $k$ has a very uniform value for neutral salts, but varies considerably for acids and bases, being high for strong acids and low for weak ones.

Regarding the dissociation values of $k$, Ostwald has separated acids, bases, and salts into three classes:

Class 1: Neutral salts, strong acids, and strong bases. The strong acids mentioned are hydrochloric, hydrobromic, hydriodic, nitric, chloric, and sulphuric; the strong bases are hydroxides of the alkali and alkali-earth metals.

Class 2: Moderately strong acids and bases. The acids are phosphoric, sulphurous, and acetic; the bases are the hydroxides of ammonium, silver, and magnesium.

Class 3: Weak acids and bases. The acids are carbonic, hydrosulphuric, hydrocyanic, silicic, and boracic; the weak bases are the hydroxides of the trivalent metals and of those divalent metals not mentioned in Classes 1 and 2.

**Applications.** — This discussion of the theories and laws of electrolytic dissociation enables us to explain many important operations and reactions in analytical chemistry, which otherwise could hardly be understood.

A few of the explanations may be conveniently formulated by questions and answers:

**1.** *How does ionization aid chemical activity?*

By dissociation of the solute into its ions, making it possible for them to combine with other ions.

**2.** *How may heat aid chemical activity?* [1]

By producing rapid vibrations of the molecules, which thus increases the speed of the reaction.

**3.** *How may dilution aid chemical activity?*

By expanding the volume, thus decreasing the pressure [2] and increasing the degree of dissociation.

4. *Why is the activity of an acid or a base usually decreased by adding some salt of that acid or base?*

Two examples are given :

(1) [1]The addition of sodium acetate to acetic acid decreases the solvent power of the acid, since the salt is more strongly dissociated than the acid, and causes a portion of the latter to reassume the molecular condition by increasing the concentration of the $C_2H_3O_2$ ions.

(2) The addition of ammonium chloride to ammonia[2] water decreases the solvent action of the latter by increasing the concentration of the $NH_4$ ions, and decreasing the dissociation and activity of the $NH_4OH$.

5. *When an excess of a normal salt of a weak acid is added to a solution of a strong acid, why is the activity of the strong acid destroyed, and that of the resulting weak acid greatly weakened?*

If an excess of sodium acetate is added to a solution of calcium phosphate in very dilute hydrochloric acid, the phosphate will be precipitated in spite of the fact that it is soluble in both hydrochloric and acetic acids. The explanation of this behavior is as follows : [3] Hydrochloric acid and sodium acetate react to form sodium chloride and acetic acid. The latter, in the presence of the excess of sodium acetate, is forced back into the inactive molecular condition in which it is no longer able to hold the phosphate in solution.

6. *Why does the addition of a solvent having an ion in common with that of a solute salt tend to precipitate the solute?*

This question already has been answered in the

explanation of the precipitation of common salt from its solution by the addition of hydrochloric acid.

7. *Why do reagents behave differently towards the same elements in different compounds?*

For example, hydrogen sulphide precipitates black cupric sulphide from a solution of cupric sulphate, but not from a solution of potassium cuprous cyanide. Another example, silver nitrate precipitates white silver chloride from a solution of potassium chloride, but not from a solution of potassium chlorate. The general answer to the question is that the chemical activity of a compound depends on its dissociated ions, — not on the presence of certain elements. Hydrogen sulphide, $H_2S$, reacts with cupric sulphate, $CuSO_4$, because the latter is ionized into Cu and $SO_4$. Hydrogen sulphide does not react with potassium cuprous cyanide, $K_3Cu(CN)_4$, because the latter gives no free Cu ions, but the molecule is dissociated into the ions, $3K$ and $Cu(CN)_4$.

In the second example silver nitrate, $AgNO_3$, reacts with potassium chloride, KCl, because the latter is dissociated into K and Cl; but silver nitrate does not react with potassium chlorate, $KClO_3$, as the latter salt is dissociated into K and $ClO_3$.

8. *Why do reagents behave alike with various salts of the same metal?*

When we say of any substance that it is a salt of a certain metal, — such as copper, — we imply that it dissociates in solution with the formation of ions of that metal. These always react alike, no matter

what the negative ions be with which they are in equilibrium.

9. *Why are normal salts usually better precipitants than their corresponding acids or bases?*

For example, calcium chloride readily reacts with ammonium carbonate, but not with carbonic acid. The following equations illustrate the comparative reactivities of normal salts, acid salts, and acids:

$(NH_4)_2CO_3 + CaCl_2$ yields an immediate precipitate;
$H(NH_4)CO_3 + CaCl_2$ yields a tardy precipitate;
$H_2CO_3 + CaCl_2$ yields no precipitate.

Normal salts are most completely dissociated, while weak acids are very slightly dissociated. Acid salts of weak acids partake of the nature of both normal salts and weak acids. As ammonium carbonate is a normal salt, it is more completely dissociated than either the acid salt, $H(NH_4)CO_3$, or the acid $H_2CO_3$, — and hence it reacts with calcium chloride more readily.

10. *Why does an excess of a strong basic precipitant redissolve many precipitates from salts of weak bases?*

For example, a weak solution of sodium hydroxide precipitates aluminum hydroxide from a strong solution of aluminum sulphate, but on adding an excess of the precipitant, the precipitate disappears. Two reactions occur here:

(*a*) Aluminum hydroxide is formed:

$6 NaOH + Al_2(SO_4)_3 = 2 Al(OH)_3 + 3 Na_2SO_4$; and on adding more sodium hydroxide the white precipitate dissolves, forming sodium aluminate, —

(*b*) $Al(OH)_3 + 3 NaOH = Na_3AlO_3 + 3 H_2O$.

Interpreted in terms of the ionic theory, aluminum being a very weak basic metal, its hydroxide is easily influenced by a strong base. In aqueous solution $Al(OH)_3$ is in equilibrium, being partly dissociated into the ions $Al^+$ and $3\ OH^-$, and, by loss of water, partly into the ions $H^+$ and $AlO_2^-$. When a strong base like NaOH is added, it neutralizes the acid $HAlO_2$, forming $Na_3AlO_3$ and water. This destroys the equilibrium, and more $H^+$ and $AlO_2^-$ are developed, only to be in turn neutralized by more NaOH. And so the process continues till all of the $Al(OH)_3$ goes into solution as $Na_3AlO_3$.

# CHAPTER III

## METHODS OF ANALYTICAL SEPARATION

**Object of Separation.** — It is only in rare cases that the chemist is able to recognize and identify individual elements or compounds in the mixtures which contain them, without having first separated them from the other bodies there present. In some cases, — the mixtures being purely mechanical, — a mechanical treatment is sufficient to accomplish the separation; in other cases, — as when the substances are present in solution, — it is necessary in addition to make use of chemical or physical processes, by which means the material under examination is converted into such form that the recognition of its elements is possible. We have therefore two classes of separations, — the members of the first class being of a mechanical nature, whereas those of the second are of either physical or chemical character. The principal separations of the first class are brought about by the operations of *decantation, filtration,* and *washing.*

### MECHANICAL SEPARATIONS

**Decantation.** — When we have a mixture of a solid with a liquid in which it is insoluble, or a mixture of two liquids which are mutually insoluble, we may

separate them by this process, provided that their specific gravities are so different that one of the compounds of the mixture will settle and separate completely from the other. From a mixture of liquid with solid, — for example, water and silver chloride, — we may remove most of the liquid by careful pouring or by suction with a pipette. From a mixture of liquids, — such as water and ether, — we may remove either layer with the pipette, or we may draw off the lower layer by means of a separatory funnel.

Though decantation never separates completely, it is convenient for the removal of the bulk of liquids from finely divided precipitates which pass through the filter paper, or from gelatinous precipitates which clog its pores. Separation can be hastened by centrifugal shaking of the mixture before decantation.

### Experiment 5

(*a*) Dissolve a few crystals of silver nitrate in 10 c.c. of water in a test-tube, and then add dilute hydrochloric acid, drop by drop, until, by shaking, the white silver chloride settles beneath a clear liquid. Decant the liquid by pouring it off with a glass rod held against the edge of the test-tube. Add more water to the solid and decant again by immersing the tip of a pipette in the clear liquid and sucking it off with the mouth (never allow the liquid to rise to the mouth). Close the mouth-end of the pipette with the tongue, lift out the pipette, and when the tongue is removed the liquid will flow out.

(*b*) Mix 5 c.c. each of ether and water in a test-tube by shaking vigorously. The lighter ether will rise to the top. Remove either the ether or water with a pipette.

**Filtration.** — Filtration is the separation of a solid *residue* from a liquid *filtrate* by means of a porous

partition impervious to the residue. The partition most frequently used in analytical work is unsized paper, supported in a glass funnel. A circular paper is folded *twice*, so as to form the quadrant of a circle, and is then fitted into a glass funnel and dampened, so as to adhere closely to the sides of the funnel. For rapid filtration it is convenient first to fold the paper once across the middle, and then to "plait" it on radial lines, so that it resembles finally a folding paper fan. On opening a paper so folded, it will be seen to fit loosely in the funnel and to leave numerous channels through which the filtrate may escape.

To prevent spattering, the beveled tip of the funnel should rest against the inside of the receiving vessel.

Three important factors determine the rate and degree of separation by filtration, namely: temperature, pressure, and the ratio between the size of the pores of the partition and the size of the particles of the residue.

Increase of temperature decreases the adhesion between the molecules of the filtrate and those of the residue, and increases the size of the colloidal granules and crystals of the residue.

Pressure needful for filtration is usually obtained through gravity, but sometimes through gravity and suction combined. The most effective method of diminishing the atmospheric pressure is the use of the suction pump. A platinum cone should be placed in the apex of the funnel to support the moistened paper, which should be so closely fitted to the sides of the funnel as to leave no air channels. The funnel tube is then to be connected with the filter flask of a suction pump.

The third factor for effective filtration consists in increasing the size of the particles of residue, or in diminishing the size of the pores of the partition. The particles of the residue are enlarged by heat and by contact with the liquid from which they are formed. Both colloidal and crystalline particles grow when immersed in a mother liquor containing smaller particles of the same kind. Hence it is the usual practice to digest the mixture for a short time before filtration.

Care should be taken, however, to keep the residue covered with liquid during the digestion, as on exposure to the air many precipitates oxidize and often redissolve in another form. The amorphous variety of ferrous sulphide obtained by precipitation with ammonium sulphide oxidizes in contact with the air to soluble ferrous sulphate.

### Experiment 6

Arrange filtering apparatus as described and filter the following mixtures: silver chloride in water, barium sulphate in water (made by adding dilute sulphuric acid, drop by drop, to a dilute solution of barium chloride), and aluminum hydroxide in water (made by adding a very dilute solution of sodium hydroxide to a concentrated solution of alum till a heavy gelatinous mass appears). Try all three mixtures with folded filters, then with creased filters, and finally with the filter pump. After all these trials, if the filtration of either mixture is very slow or the filtrate remains muddy, try decantation first, and then filtering the moist residue with the pump.

**Washing.** — Neither decantation nor filtration will thoroughly cleanse the residue from the filtrate. It is necessary in most cases to *wash* off the adhering filtrate

by pouring on water, or water made acid, alkaline, or salt, according to the nature of the residue. When a thorough separation is demanded, the washing should continue till the washings no longer show a trace of the solutes of the filtrate. In many separations, where the residues are liable to oxidation on exposure to the air, it is necessary to hasten the washing with the pump.

Two rather serious difficulties are frequently encountered both in washing and in filtration; namely, the clogging of the paper with certain finely divided residues, and the tendency of such residues to pass through the paper. As both difficulties are due to the same cause, the same treatment will correct both. The troublesome residues are colloidal in nature and, as has been stated, their particles unite or coagulate on heating. Hence it is well to subject the mixture to quiet heat — not boiling — long enough to allow the precipitate to settle to the bottom; decant the supernatant liquid into a filter and apply the pump; add warm water to the residue; and, after settling, decant and filter again in like manner. Repeat the washing by decantation once or twice, and then add the solid to the paper, finally washing directly on the paper.

As colloidal substances are somewhat soluble in water, but less soluble in many neutral salt solutions, the latter are frequently used for washing. It is also necessary in special cases to use acid or akaline solutions for washing.

As regards the effectiveness of washing, Ostwald gives this calculation: " Should the washing liquid amount to nine times as much as the original moisten-

ing solution, and should 1 gram of foreign substance be mixed with the precipitate to begin with, then after four washings only $(\frac{1}{10})^4$ gram, *i.e.* 0.0001 gram, of the impurity would remain."

### Experiment 7

(*a*) Wash the residue of barium sulphate (last experiment) with water till the washings show no white precipitate with drops of barium chloride solution.

(*b*) Precipitate some ferric hydroxide by adding ammonium hydroxide to a boiling solution of ferric chloride till the latter is permanently alkaline. Filter and wash according to directions above.

#### PHYSICAL AND CHEMICAL SEPARATIONS

The second class of separations, to which reference was made on p. 26, includes *solution, precipitation, evaporation,* and *ignition.*

Solution. — Most methods of separation are more or less dependent upon solution as their starting point, and in some cases separation is completed by this operation. Solids composed of two or more substances, like minerals and alloys, may be separated in this manner when only a part of their constituents is soluble.

### Experiment 8

(*a*) Finely powder a small piece of dolomite in an agate mortar, and dissolve by warming with dilute hydrochloric acid. The small residue insoluble in the acid is silica, whose separation may be completed by filtration.

(*b*) Dissolve some filings of soft solder in a test-tube, in a mixture of equal parts of nitric acid and water, and when the

action ceases, add some water. When the white powder has settled, pour off the clear liquid into a small dish and evaporate to dryness. Try to dissolve the residue in the test-tube by boiling with water. Soft solder is an alloy of tin and lead, and by solution of the lead in nitric acid the two metals are separated.

The ordinary solvents for solids are water, hydrochloric acid, nitric acid, and aqua regia.

A small portion of the powdered solid is treated in a test-tube with cold water. If the solid does not disappear after shaking the contents several times at intervals, transfer a drop of the solution to a watch glass with a glass rod. Place also a drop of distilled water on the watch glass near that of the solution. Heat the watch glass on an asbestos board or sand bath to dryness. Compare the residues left from the two drops. If both are alike in size, cold water does not dissolve the solid; but if the residue from the supposed solution is larger, the solid is at least partly soluble in water. In either case boil the contents of the test-tube, and if the solid still does not disappear, again evaporate a drop of the solution to dryness on the watch glass. A large residue indicates a partial solubility of the solid in hot water.

Treat another portion of the powdered solid in a similar manner in succession with dilute and concentrated hydrochloric acid, dilute and concentrated nitric acid, and aqua regia. If the substance dissolves completely in any one of the solvents, the solvents following need not be used.

Sometimes a solid is composed of different substances which have no solvent in common. One substance may

dissolve only in water, another only in hydrochloric acid, another only in nitric acid, etc. In such extreme cases it is necessary to separate the mixed solids by means of solvents. Some substances cannot be dissolved by any of the reagents mentioned. It is necessary in such cases to fuse them with an alkaline carbonate in a platinum crucible or foil, and afterwards to digest the fused mass with water. (See directions for fusion, p. 43.)

### Experiment 9

(a) Using the methods described above, dissolve .5 gram of each of the following substances: cupric sulphate, barium sulphate, and sand.

(b) Mix .5 gram each of the same substances and separate them by solution.

**Precipitation.** — The terms *soluble* and *insoluble*, as used in practice, have only relative values; and they merely indicate considerable differences in degree of solubility, for, in fact, all substances are soluble. We have seen in Exp. 1 that a substance which is in complete solution at one temperature may be rendered less soluble and thrown out of solution by change to another temperature. And we also have seen that a material whose solubility appears to be about the same at all temperatures may be thrown out of solution by modifying the solvent in such a manner as to decrease its solubility therein. When by either of these means we have forced a solution to give up a part of its solute in solid form, we have performed the operation of *precipitation;* and the solid thrown down is called a *precipitate.* In

## TABLE I — SOLUBILITIES

| | Acetate | Arsenate | Arsenite | Borate | Bromide | Carbonate | Chlorate | Chloride | Chromate | Cyanide | Ferrocyanide | Ferricyanide | Fluoride | Hydroxide | Iodide | Nitrate | Oxalate | Oxide | Phosphate | Silicate | Sulphate | Sulphide | Sulphite | Tartrate | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ag | 1 | 2 | 2 | 2 | 3 | 2 | 1 | 3 | 2 | 3 | 3 | 1 | | 3 | 1 | 2 | 2 | 2 | | 4 | 2 | 2 | 2 | | Ag |
| Hg' | 4 | 2 | 2 | 2 | 6 | 2 | 1 | 6 | 2 | | | | | 2 | 1 | 2 | 2 | 2 | | 4 | 2 | 2 | 4 | | Hg' |
| Pb | 1 | 2 | 2 | 2 | 5 | 2 | 1 | 5 | 6 | 2 | 2 | 4 | 2 | 2 | 4 | 1 | 2 | 2 | 2 | 2 | 6 | 2 | 2 | 2 | Pb |
| Hg'' | 1 | 2 | 2 | | 1 | 2 | 1 | 1 | 4 | 1 | | | 4 | | | 2 | 1 | 2 | 2 | 2 | | 1 | 2 | 2 | 2 | Hg'' |
| Bi | 1 | 2 | | 2 | 4 | 2 | 1 | 4 | 2 | | | 1 | 2 | 2 | 1 | 2 | 2 | 2 | | 1 | 2 | 2 | 2 | | Bi |
| Cu | 1 | 2 | 2 | 1 | 2 | 1 | 2 | 1 | 1 | 1 | 2 | 3 | | 2 | 2 | 1 | 1 | 2 | 2 | 2 | 2 | 1 | 2 | 1 | 1 | Cu |
| Cd | 1 | 2 | | 4 | 1 | 2 | 1 | 1 | 2 | 2 | | 4 | 2 | 1 | 1 | 2 | 2 | 2 | 2 | 1 | 2 | 1 | 4 | | Cd |
| Sn | 1 | | 2 | | 1 | 1 | 2 | | 3 | 3 | 1 | 2 | 1 | | 2 | 2 | 2 | | 1 | 2 | 1 | 2 | | Sn |
| Sb | | 2 | 2 | | 4 | | | 4 | 2 | | 1 | 2 | 4 | | 2 | 2 | 4 | | 2 | 2 | 2 | 1 | | Sb |
| As | | | 1 | | 1 | | | | | 1 | 1 | 1 | 1 | | 3 | 2 | | 2 | | As |
| Fe'' | 1 | 2 | 2 | 2 | 1 | 2 | 1 | 1 | | 6 | 3 | 3 | 4 | 2 | 1 | 1 | 2 | 2 | 2 | 2 | 1 | 2 | 1 | 4 | Fe'' |
| Fe''' | 1 | 2 | 2 | 2 | 1 | | 1 | 1 | 1 | | 3 | 1 | 1 | 2 | 1 | 1 | 2 | 2 | 2 | 2 | 1 | 2 | 1 | 1 | Fe''' |
| Cr | 1 | 2 | | 2 | 5 | 2 | 1 | 5 | 2 | 2 | | 1 | 2 | 1 | 1 | 4 | 6 | 2 | 2 | 4 | 6 | 1 | 1 | 1 | Cr |
| Al | 1 | 2 | | 2 | 1 | | 1 | 1 | | 1 | 2 | 1 | 1 | 2 | 2 | 2 | 2 | 1 | 2 | 2 | 1 | Al |
| Co | 1 | 2 | 2 | 2 | 1 | 2 | 1 | 1 | 2 | 6 | 3 | 3 | 4 | 2 | 1 | 1 | 2 | 2 | 2 | 2 | 1 | 2 | 1 | 1 | Co |
| Ni | 1 | 2 | 2 | 2 | 1 | 2 | 1 | 1 | 2 | 6 | 3 | 3 | 4 | 2 | 1 | 1 | 2 | 2 | 2 | 2 | 1 | 2 | 2 | 2 | Ni |
| Mn | 1 | 2 | 2 | 2 | 1 | 2 | 1 | 1 | 1 | 2 | 2 | 3 | 2 | 1 | 1 | 4 | 2 | 2 | 2 | 1 | 2 | 2 | 4 | Mn |
| Zn | 1 | 2 | | 2 | 1 | 2 | 1 | 1 | 1 | 2 | 6 | 2 | 4 | 2 | 1 | 1 | 2 | 2 | 2 | 2 | 1 | 2 | 1 | 2 | Zn |
| Ba | 1 | 2 | 2 | 2 | 1 | 2 | 1 | 1 | 2 | 4 | 4 | 6 | 1 | 1 | 1 | 2 | 2 | 2 | 3 | 1 | 2 | 2 | Ba |
| Sr | 1 | 2 | 2 | 2 | 1 | 2 | 1 | 1 | 4 | 1 | 1 | 6 | 1 | 1 | 1 | 2 | 1 | 2 | 2 | 5 | 1 | 2 | 2 | Sr |
| Ca | 1 | 2 | 2 | 2 | 1 | 2 | 1 | 1 | 4 | 1 | 1 | 6 | 4 | 1 | 1 | 2 | 4 | 2 | 2 | 5 | 1 | 1 | 2 | Ca |
| Mg | 1 | 2 | 2 | 4 | 1 | 2 | 1 | 1 | 1 | 1 | 6 | 2 | 1 | 1 | 4 | 2 | 2 | 2 | 1 | 2 | 1 | 2 | Mg |
| Na | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | Na |
| K | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | K |
| Li | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | Li |
| NH₄ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | | 1 | 1 | 1 | 1 | NH₄ |

KEY TO TABLE. — 1 = soluble in water; 2 = soluble in acids only; 3 = insoluble in acids and water; 4 = sparingly soluble in water, easily soluble in acids; 5 = sparingly soluble in water and acids; 6 = sparingly soluble in acids only.

the two cases cited the separation is of physical nature; for, apart from a decrease in the degree of dissociation, no chemical change has been worked upon the solute. There are cases, however, which are more common in the practice of analytical operations, in which the physical separation is accompanied with or preceded by chemical changes without which the precipitation would not occur. Such cases involve reaction between the solute and some added material, called the *precipitant;* and the principle governing such reaction is that the ions representing that part of the solute whose separation is desired, combine with certain ions of the precipitant to form a new compound which is less dissociated and less soluble than either the solute or precipitant. So soon as enough of the new and less soluble compound has been formed to saturate the solution, the excess which is formed is obliged to separate in the form of a precipitate.

Precipitation is, therefore, the result of supersaturation, brought about either by chemical or physical means; but it does not always take place immediately upon the occurrence of supersaturation. Frequently we are obliged to resort to various devices — such as heating, cooling, shaking, or stirring— to induce it to begin.

**Theories of Precipitation.**— The early chemists believed that chemical reactions are governed solely by chemical affinity. Bergman (1775) taught that when two compounds, $MX$ and $NY$, are brought together, if the affinity of $M$ is greater for $Y$ than for $X$, there will be a complete metathesis: $MX + NY = MY + NX$. For

example: if solutions of barium chloride and sodium sulphate were brought together in suitable proportions, there should be complete precipitation of the insoluble barium sulphate, because of the greater affinity of barium for sulphuric acid than for hydrochloric acid. According to Bergman's theory, reaction in the reverse direction should not take place; that is, barium sulphate should not be decomposed by treatment in the presence of water with some substance like sodium carbonate, for whose acid constitutent barium had less affinity than for sulphuric acid, with which it already was united.

Berthollet (1804) afterwards demonstrated that Bergman's theory is true only in part, and that there is a metathesis between barium sulphate and sodium carbonate, provided a large excess of the latter is used. He announced the theory that chemical reactions depend upon two things, — relative chemical affinity and relative mass, — and embodied the theory in the following laws, which bear his name: —

1. *When solutions of different substances are mixed, and a substance volatile under existing circumstances can be formed, it is formed and escapes.*

2. *When solutions of different substances are mixed, and a substance insoluble under existing circumstances can be formed, it is formed and separates.*

The modern theory of dissociation enables us to form a clearer conception of these precipitation phenomena which result from chemical action. As was said on p. 19, the formation of an insoluble compound is due to the union of ions, from the considerably disso-

ciated solute and precipitant to a body whose dissociation and solubility are relatively less.

In the case of barium chloride and sodium sulphate we have in solution, before the materials are mixed, molecules of $BaCl_2$ in equilibrium with ions of Ba and Cl, and molecules of $Na_2SO_4$ in equilibrium with ions of Na and $SO_4$. Upon mixing, the Ba and $SO_4$ ions are given the opportunity for combination.

Now the solubility of $BaSO_4$ is very slight; *i.e.*, the concentration of its solution, when the solute is in equilibrium with solid $BaSO_4$, is very low. Yet this concentration is made up of the values $c$, the concentration of the undissociated portion, and of $a$ and $b$, the concentrations of the Ba and $SO_4$ ions;[1] and we have seen that $a.b = k.c$. It will be understood that no more Ba and $SO_4$ ions can simultaneously exist in one solution than will satisfy this equation; and therefore these ions, whose concentrations in the solutions of barium chloride and of sodium sulphate were very considerable, must unite until the equation is satisfied; and as the sum of the concentrations $c$ and $b$ and $a$ is very small, solid barium sulphate will be separated until equilibrium has been restored. But as fast as the ions of Ba and $SO_4$ are thus withdrawn from solution further portions of $BaCl_2$ and $Na_2SO_4$ are dissociated; and so the reaction continues until either all of the Ba or all of the $SO_4$ in excess of that permitted by $a.b = k.c$ has been used up.

The solubility of the barium sulphate is lessened by the presence of an excess of either a soluble salt of

[1] For discussion of this relation, refer to pp. 18–20.

barium or of sulphuric acid. An increase in the con-
centration of either the Ba or the $SO_4$ ions will reduce
the proportion of the dissociated salt, and consequently
the amount in solution.

Since an excess of reagent often vitiates the reaction,
it is advisable to add the precipitant solution slowly, so
as to be able to follow the course of the reaction and
to avoid error.

### Experiment 10

(*a*) In two test-tubes put a solution of silver nitrate. To the
first add very little dilute ammonia, drop by drop, shaking the
test-tube after each drop. To the second add ammonia directly
without dropping.

(*b*) In each of the test-tubes put a very dilute solution (1 : 500)
of silver nitrate. To the first add concentrated hydrochloric acid
and boil. When the white precipitate disappears add water.
To the second add dilute hydrochloric acid and boil.

**Evaporation.** — Evaporation is the removal of part or
the whole of a liquid by volatilization. It is sometimes
accomplished by exposure to the open air or to the sun
in flat vessels; but for analytical purposes this pro-
cedure is too slow, and application of artificial heat is
necessary. When very rapid evaporation is desired
and proper care is exercised to remove the vessel when
the residue is quite dry, the operation may be carried
out in an open dish on a sand bath, or on an iron or
asbestos plate, over the direct flame. The dangers of
spattering and of overheating the residue have put this
method somewhat in disrepute. The safest and most
satisfactory method in all respects is the use of liquid
baths. Water or steam baths are most frequently used;

but for evaporations requiring high temperatures, oil and paraffin baths are sometimes employed. In laboratories supplied with water pressure and fixtures, water baths should be supplied with constant level apparatus to prevent drying. All evaporations of active reagents should .be conducted under a hood or out of the laboratory.

As a means of analytical separation, evaporation may be partial only, as when a dilute solution is to be concentrated; or it may be complete, as when a solid solute is to be recovered from its solution.

### Experiment 11

(*a*) Make a weak solution (1 : 100) of cupric sulphate. Evaporate on a water bath down to one-fourth and allow it to cool.

(*b*) Repeat (*a*) with a similar solution of calcium chloride. If crystals fail to appear, evaporate to dryness on an asbestos plate.

**Ignition.** — This process consists in the application of intense heat to solid bodies, and has for its purposes:

1. The separation of gases from solids, as when calcium carbonate is converted into calcium oxide through the removal of carbon dioxide.

2. The separation of liquids from solids, as when salts are ignited for the removal of their water of crystallization.

3. The separation of solids from solids, as when the readily volatile ammonium compounds are driven off from less volatile salts.

*The Bunsen Lamp.* — The sources of heat for ignition in the analytical laboratory are the ordinary gas

lamps — usually Bunsen's type — and the blast lamp. By means of a perforated thimble and a stopcock both the air and gas supplies can be regulated in a Bunsen burner. An excess of gas gives a luminous flame rich in unconsumed carbon, while an excess of air produces a non-luminous blue flame.

The flame is composed of three zones — an outer zone of hot oxidized gases mixed with oxygen, a medial zone of hot reduced gases mixed with unconsumed carbon, and an inner dark zone of cool unconsumed gases. The high temperature and the free oxygen render the outer zone favorable to processes of oxidation, and it is therefore called the oxidizing flame. The medial zone, with its highly heated unconsumed carbon, is the reducing flame. The hottest part of the flame is the junction of the reducing and oxidizing zones, where oxidation is most vigorous.

*The Blowpipe.* — For convenience in application of the different parts of the flame a blowpipe is often used. The type of this instrument is a small tube about 20 cm. long with a mouthpiece at one end and a nozzle tip of brass or platinum at the other end. The nozzle end is usually bent perpendicular to the shaft of the blowpipe. A constant blast of air is fed into the flame by using the cheeks as a bellows, without interfering with the regular breathing. If the cheeks are distended, air can be forced out of the mouth by their contraction at the same time when inspiration is being effected through the nose. To acquire the proper and efficient use of the blowpipe some practice is necessary.

To obtain the best results the air holes at the base of the Bunsen burner are closed so as to give a small luminous flame. It is best to insert into the burner tube a smaller and somewhat longer tube, compressed and beveled at the top. This flattens the flame ; and the oblique edge is convenient to the operator, since the flame is commonly directed downwards. For oxidation the tip of the blowpipe is placed just inside the flame ; and with a strong blast the extreme tip of the flame is made to impinge on the object to be oxidized. For reduction the tip is placed on the edge of the flame and, using a moderate blast, the center of the flame is allowed to play upon the object to be reduced.

### Experiment 12

(*a*) Heat a small piece of metallic lead on a piece of charcoal with the oxidizing flame. Notice the yellow film of metallic oxide on the lead.

(*b*) Heat some lead acetate on charcoal with the reducing flame to quiet fusion. When cold, pick out the metallic lead and test its malleability on the anvil.

*Blast Lamp.* — When higher temperatures are desired than can be produced by the Bunsen lamp or mouth blowpipe, the blast lamp is employed. It consists essentially of two concentric tubes, of which the outer and larger conveys the gas, while the inner and smaller supplies the air which is furnished under pressure by a bellows or water blast.

*Crucibles.* — The crucibles in common use are small cup-shaped vessels of porcelain or platinum ; for

special purposes they may be made of silver, graphite, iron, etc.

The method of applying the heat is to place the crucible on a platinum or pipe-clay triangle supported on a ring stand. The ring is elevated at first, so that the flame will not heat the crucible too rapidly. Afterward the ring is lowered, or the flame elevated, so as to obtain the required heat.

For testing small amounts of material, fragments of porcelain, mica or asbestos plates, or small platinum foils (about 2 cm. square) are used instead of crucibles. It is necessary to observe the following precautions in using crucibles : —

(*a*) Do not heat or cool a porcelain crucible too quickly, as in either case it is liable to crack.

(*b*) Apply only the outer non-luminous flame to a platinum crucible; never a yellow-white flame, or the interior blue zone of the flame, as the one contains unconsumed carbon, and the other acetylene gas, which is easily decomposed into hydrogen and carbon. At high temperatures platinum unites with carbon to form the carbide of platinum, which will oxidize later, and cause the metal to blister.

(*c*) Always handle a hot platinum crucible with platinum tongs, and support it on a platinum or pipe-clay triangle.

(*d*) Never ignite the following substances in platinum crucibles : metals, salts of easily reducible metals (those of lead, silver, copper, arsenic, etc.), substances evolving chlorine or bromine, sulphites, phosphates in presence of organic matter, and the nitrates, cyanides, and hydroxides of the alkalies and alkaline earths.

All of these readily corrode platinum. In case the substance to be analyzed is of unknown character, it should be tested first on a piece of platinum foil.

(*e*) The platinum crucible can be cleaned by rubbing the surface with moist sea sand, applied with the finger. Persistent stains are generally removed by concentrated hydrochloric or nitric acid, or by fusion with borax or acid potassium sulphate. If the latter substance is used, allow the fused mass to cool and then dissolve in water. Do not attempt to break out the mass, as bending is injurious to platinum ware.

**Fusion.** — In theory, fusion is identical with solution. As has been pointed out, a solvent is essential to the chemical reaction of soluble substances, in order that they may be brought into intimate contact ; and, similarly, a flux is essential to the chemical reaction of substances subjected to fusion. The flux may be a negative substance and not enter into the reaction, but merely act as a solvent; *e.g.*, fluor spar in metallurgical operations ; or the same substances may act both as a solvent and as a chemical reagent; *e.g.*, borax fused with certain metallic oxides. The fluxes most frequently used in analytical operations are sodium carbonate, potassium cyanide, potassium nitrate, borax, microcosmic salt, and acid potassium sulphate. Often, combinations of some of these salts are used.

The so-called *fusion mixture* is composed of sodium and potassium carbonates, mixed in the proportion of their molecular weights. The mixed salts melt at a lower temperature than either of the individuals. For fusion and oxidation, a mixture of sodium carbonate

and potassium nitrate is employed; for fusion and reduction, a mixture of sodium carbonate and potassium cyanide.

### Experiment 13

(*a*) Mix intimately some powdered insoluble manganese dioxide with twice its bulk of fusion mixture, and heat to quiet fusion on a platinum foil with the oxidizing flame. When cold, dissolve the green mass in water.

(*b*) In (*a*) substitute chromic iron for manganese dioxide, and in addition to the fusion mixture use an equal bulk of potassium nitrate.

(*c*) In (*a*) substitute feldspar or clay for manganese dioxide, and acid potassium sulphate for the fusion mixture.

**Heating in Closed Tubes.** — Crucible ignition is generally an oxidation process, but closed tube ignition is different inasmuch as the length of the tube excludes the oxygen of the air and prevents oxidation. Thus the closed tube is used for reduction. The tube is usually made of small, hard glass tubing, about .5 cm. in diameter and 10 cm. long. First cut the tube to the proper length, and then heat one end of it in the blowpipe flame till it is closed and well rounded off. While red hot take it out of the flame and, holding it vertically downward, blow steadily till a small bulb is formed.

For use, the bulb is about half filled with the substance, or with the substance mixed with a flux or reducing agent; and it is heated first with the smoky flame to expel the moisture at a low temperature. Often this heating is sufficient, but if a very high temperature is required, the non-luminous flame must be applied and the tube heated to the desired degree.

### Table II — Behavior of Substances heated in a Bulb-Tube [1]

| | |
|---|---|
| 1. Substance fuses and solidifies again . . . | Compounds of alkalies and of alkaline earths. |
| 2. Substance does not fuse, but changes color: | |
| (a) Chars and evolves carbon dioxide . . | Organic substances. |
| (b) Yellow while hot, white on cooling . . | Zinc oxide. |
| (c) White while hot, brown on cooling . . | Bismuth oxide. |
| (d) White while hot, yellow on cooling . . | Lead oxide. |
| (e) Orange while hot, yellow on cooling . . | Tin oxide. |
| 3. Substance gives off water . . . . . . | Water of crystallization or constitution. |
| 4. Substance sublimes . . . . . . . . | Ammonium salts. Arsenic " Antimony " Mercury " Sulphur. |
| 5. Substance gives off a gas: | |
| (a) Violet vapors . . . . . . . . . | Iodine and iodides. |
| (b) Red fumes of nitrogen oxides . . . | Nitrates of heavy metals. |
| (c) Oxygen (tested with glowing match) . | Chlorates and nitrates. |
| (d) Carbon dioxide (tested with lime water) | Carbonates of heavy metals. |
| (e) Sulphur dioxide (detected by odor) . . | Sulphur compounds. |
| (f) Cyanogen (odor of almonds) . . . . | Cyanides. |

### Experiment 14

(a) Heat some zinc sulphate in a bulb-tube, using the luminous flame first and then increasing the heat to dull redness. Examine carefully, for all changes; — whether water is given off, the color of the salt while hot and when cold, etc.

(*b*) In a bulb-tube heat some lead nitrate. Test the gas from the bulb with a glowing splinter and note the color, odor, etc., of the gas. Also notice the behavior of the solid substance.

(*c*) Heat some sodium acetate in a bulb and notice the odor of the evolved gas, and the change in the solid.

(*d*) Heat some ammonium carbonate in a bulb. The salt *sublimes* and collects on the cold part of the tube.

**Platinum Wire; the Bead Tests.** — The platinum wire is used in two sets of tests — those for simple flame coloration and those for bead coloration. Flame coloration will be discussed under another head.

Certain easily fusible acid salts, such as acid potassium sulphate and borax, have the power of displacing volatile acids and of combining with metallic oxides to form fusible sulphates, phosphates, and borates.

It happens that many metals impart distinctive colors to their fused mixtures with these salts, and that they may often be identified by this means. A platinum wire, provided with a glass handle and looped at the free end, serves as a support for a bead of fused borax or other fused acid flux. The loop of the clean wire is heated to redness, dipped into the powdered flux, and heated in the non-luminous flame till the loop is filled with a clear bead. A very small piece of the substance to be analyzed is stuck to the soft bead, and is then heated with the blowpipe, first with the oxidizing, then with the reducing, flame. It is necessary to continue the blast till the substance becomes thoroughly incorporated in the bead. During the operation the following observations should be made : whether the substance fuses, whether the bead becomes transparent or remains

cloudy, the color of the bead, and its behavior in the oxidizing and reducing flames.

### Experiment 15

(*a*) Make borax bead[1] tests in both the oxidizing and reducing flames with thin pastes of cobalt nitrate, chromium nitrate, and ferrous sulphate.

(*b*) Fuse a small bit of glass in a bead of microcosmic salt. The floating silica constitutes the *skeleton bead*, a test for silicates.

TABLE III — BEHAVIOR OF SUBSTANCES FUSED IN BORAX OR MICROCOSMIC SALT

| OXIDIZING FLAME | REDUCING FLAME | |
|---|---|---|
| 1. Blue . . . . . . | Blue . . . . . | Cobalt salts. |
| 2. Green . . . . . . | Green . . . . | Chromium salts. |
| 3. Yellow . . . . . | Dark green . . | Iron salts. |
| 4. Amethyst . . . . | Colorless . . . | Manganese salts. |
| 5. Dark yellow . . . | Gray . . . . . | Nickel salts. |
| 6. Green (hot), blue (cold) | Red or colorless . | Copper salts. |

**Charcoal.** — Charcoal, as a support for ignition, possesses the following properties: it is a reducing agent and greatly facilitates reduction processes; it is infusible and has a low conducting power, and hence forms an ideal crucible; and since it is porous, it absorbs the excess of fluxes and leaves the infusible substances on the surface. It is used in blowpipe analysis as a support and reducing agent combined. A small conical pit is bored with a knife blade or iron forceps handle near one end of a piece of even grain, and the substance, or

mixture of the substance and a flux, is placed in the pit and heated in the reducing flame with a blowpipe.

### Experiment 16

(*a*) Heat a small crystal of potassium nitrate on charcoal with the blowpipe. It will flash up and consume some of the charcoal. This kind of explosive combustion is called *deflagration.*

(*b*) Heat some lead oxide (litharge) with three times its weight of fusion mixture and a little potassium cyanide on charcoal with the blowpipe. After fusion continue to heat till globules appear. When cold, pick out the largest globule and test its malleability on the anvil.

(*c*) Heat some zinc oxide with fusion mixture on charcoal with the blowpipe. Note the color of the flame and the color of the incrustation around the pit while hot and when cold. Moisten the incrustation with a few drops of a dilute solution of cobalt nitrate and heat again. Note the color of the mass.

### TABLE IV — BEHAVIOR OF SUBSTANCES HEATED ON CHARCOAL ALONE

| | |
|---|---|
| 1. Substance deflagrates | Nitrates, chlorates. |
| 2. Substance fuses and is absorbed in charcoal | Alkali salts. |
| 3. Substance is infusible and incandescent | Alkali-earth and earth salts. |
| 4. When infusible, as in 3, treat with cobalt nitrate and heat : | |
| (*a*) Blue | Aluminum oxide and phosphates. |
| (*b*) Green | Zinc oxide. |
| (*c*) Pink | Magnesium oxide. |
| 5. Substance leaves incrustation : | |
| (*a*) White with garlic odor | Arsenic compounds. |
| (*b*) White without odor | Ammonium and mercury compounds. |
| (*c*) Yellow (hot), white (cold) | Zinc oxide. |
| (*d*) Brown | Cadmium oxide. |

TABLE V — BEHAVIOR OF SUBSTANCES HEATED ON
CHARCOAL WITH FLUX

| | |
|---|---|
| 1. A metallic bead is left: | |
|   (a) Soft and malleable and leaves yellow incrustation . . . . . . . . . . . . . | Lead. |
|   (b) Soft and malleable and leaves white incrustation . . . . . . . . . . . . . | Tin. |
|   (c) Hard and malleable and leaves no incrustation . | Silver. |
|   (d) Hard and brittle and leaves white incrustation | Antimony. |
|   (e) Hard and brittle and leaves yellow incrustation . . . . . . . . . . . . . | Bismuth. |
| 2. Magnetic particles . . . . . . . . . . . | Iron. Nickel. Cobalt. |
| 3. Red particles . . . . . . . . . . . . | Copper. |
| 4. When the moistened fused mass blackens a silver coin . . . . . . . . . . . . . . . | Sulphur compounds. |

# CHAPTER IV

## FLAME COLORATION AND SPECTROSCOPY

**Light and Color.** — Light is due to vibrations of the ether, of great velocity, in directions perpendicular to the path of the light, and of frequencies which are inversely proportional to the lengths of the ether waves. The vibrations of lowest frequency and greatest length give rise to light of a red color. With increasing frequency, the color changes successively to orange, yellow, green, blue, and violet, the last tint being due to the shortest vibrations which can produce any effect upon the eye. Ordinary white light — such as is emitted by the sun, by the glowing carbon of a flame or electric lamp, or by the incandescent mantle of the so-called "Welsbach burner" — is made up of vibrations of all lengths, the particular quality of the light being dependent on the proportions in which the vibrations of different lengths are mingled.

All incandescent solids emit a white light whose character is dependent upon their temperature rather than on their nature; and hence we cannot well characterize solids by their appearance when incandescent. Gases and vapors, on the other hand, present distinctive colors when heated to the point of incandescence, and they may be identified by means of their color characteristics.

**Flame Colorations.** — These colors may be readily observed in the following manner: a platinum wire, bent into a

small loop at one end, and fixed in a handle of glass rod at the other, is dipped into a strong solution of the material whose vapor color is to be investigated, and is then held in the non-luminous flame of a Bunsen lamp. According to the nature of the material, the portion of the flame above the wire may be colored more or less intensely. Common salt, so treated, imparts a brilliant yellow hue to the flame; all other salts of sodium behave in similar fashion, and therefore this "flame," being given by no other substances, is taken as being characteristic of sodium. Treated similarly, potassium compounds produce a violet coloration, calcium salts a yellowish red, etc.

### Experiment 17

Guided by the above description, confirm the following statement regarding flame colorations:

### TABLE VI — SIMPLE FLAME COLORATIONS

| | |
|---|---|
| 1. Yellow, obscured by blue glass [1] . . . . | Sodium salts. |
| 2. Violet, not obscured by blue glass . . . | Potassium salts. |
| 3. Carmine-red . . . . . . . . . . | Lithium salts. |
| 4. Yellow-red . . . . . . . . . . | Calcium salts. |
| 5. Deep red . . . . . . . . . . | Strontium salts. |
| 6. Green . . . . . . . . . . . | { Barium salts. <br> Copper salts. <br> Boric acid. |
| 7. Blue . . . . . . . . . . . | { Lead salts. <br> Arsenic compounds. <br> Copper chloride. |

[1] The violet flame of potassium salts is so much less luminous than the sodium flame that the naked eye may fail to detect it in presence of the latter. But whereas the sodium flame is mostly obscured when viewed

**Spectroscopy.** — The vibrations of which we assume light to be made up follow one another through the ether in perfectly straight lines so long as their paths are not obstructed. A line of such vibrations we call a *ray;* a group of parallel rays, a *beam.* When the path of ray or beam is obstructed, a variety of things may happen according to the nature of the obstruction. In case the obstruction is pervious to the passage of the ray, a portion of the vibrations may be reflected, and the remainder will pass on through the obstruction. Such rays as have met the surface of the latter exactly at right angles will pass straight on; but any which have met it obliquely may be more or less deflected or *refracted* from the prolongation of their former path. The degree of this refraction will be governed : —

(1) by the relation between the optical " densities " of the media through which the ray is passed;

(2) by the vibration frequency or " wave length " of the ray.

When a beam of white light is passed obliquely from the air into a denser material, such as glass, there will be a dispersion of its rays, those of the shortest wave lengths being bent most from their original direction, so that the former beam of parallel rays will be spread out into a wedge of colored light, progressing from red at one edge to violet at the other. When the glass is in the form of a triangular prism, the dispersion will be most perfect; and with the help of such

through a slide of cobalt glass, that of potassium is very slightly dimmed. Accordingly, when sodium is present, it is always necessary to examine the flame for potassium with the aid of the blue glass.

a prism, we may study the character of light from any source. Obviously, if our light is white, it will be dispersed into a continuous band or "spectrum"; if it is colored, we shall have strips of color whose character will indicate the composition of the light under examination. If our beam is entirely made up of vibrations of only a few frequencies, we shall have a spectrum consisting of a few bright lines.

Spectra can also be produced by gratings of numerous thin parallel wires or of fine parallel etchings on glass or metal. If light from a narrow slit is viewed through gratings parallel with the slit, some of the light can be seen to pass unaffected while part of it produces a colored spectrum on each side of the grating. Spectra thus produced are due to *diffraction*.

**The Spectroscope.** — Two classes of instruments depending, respectively, on refraction and diffraction are used for the analysis of light. Each class has its advantages and disadvantages. The prism spectroscope produces brighter spectra, as only a small portion of the light is lost by reflection and absorption. In the case of the grating spectroscope, some light passes unaffected between the gratings, some is destroyed by interference, and only the remainder is diffracted.

For accuracy the grating spectroscope is preferable for two reasons : first, the dispersions of the rays in grating spectra are directly proportional, while those of the prism spectra are inversely proportional to the wave lengths ; and, second, the lengths of the prism spectra are dependent on the material of the prism, which accounts for the fact that no two prisms give uniform

dispersions. But the prism spectroscope, though less accurate for technical physical work, is simpler and better adapted to ordinary chemical analysis.

A simple form of the prism spectroscope consists of a refracting prism, or set of prisms, and three small telescopes mounted on a metal tripod. One of the telescopes, called the collimator, has at one end a vertical slit of adjustable width. The rays of light, having passed through the slit and been rendered parallel by the lens of the collimator, are refracted and dispersed by the prism; and the resulting spectrum is observed through the eyepiece of the second telescope. The third telescope contains a horizontal millimeter scale reduced about one-fifteenth. Light from a white flame, placed in front of the scale telescope, passes through the scale and is reflected on that face of the prism which stands before the eye telescope, so that both the image from the collimator and that from the scale are seen at the same place.

Another form of this type of instrument is the direct-vision spectroscope, in which one telescope is used for both the eyepiece and collimator, the prisms being placed within it. The Janssen direct-vision telescope,[1] made by the Geneva Society, contains also a scale telescope.

**Kinds of Spectra.** — The spectroscope shows three kinds of spectra : —

1. The Continuous Spectrum, produced by a white-hot solid or liquid. Solids and liquids emit rays of many wave lengths and thus give the colors blended in the order of their wave lengths. A platinum wire

heated to whiteness in a non-luminous flame shows a continuous spectrum in the spectroscope.

2. The Discontinuous Spectrum, produced by an incandescent gas or vapor. Gases and vapors emit rays of few wave lengths, and hence the spectrum shows only certain bright lines or bands. A platinum wire dipped in a paste of common salt and hydrochloric acid, and heated in a non-luminous flame, shows, in addition to the continuous spectrum of the white-hot wire, a bright yellow line produced by the vapors of the salt.

3. The Absorption Spectrum, produced by an incandescent solid or liquid which is viewed through a gaseous or liquid medium. The medium absorbs the rays peculiar to itself, and thus produces certain dark lines in the continuous spectrum. The so-called Frauenhofer's lines — dark bands which cross the solar spectrum — are caused by the absorption of rays emitted from the interior mass of the sun in their passage through an exterior gaseous envelope. Similarly, in the same way, white light passed through a solution of potassium permanganate gives a spectrum deprived of the yellow, green, and blue rays, in whose places are seen dark bands.

**Flame Spectra.** — Those solids which vaporize at the temperature of a Bunsen flame can easily be examined in the flame. They are the salts of the alkali and the alkali-earth metals. A blank analysis should first be made by holding a clean platinum wire in the dark flame about 2 cm. before the collimator slit. By focusing the telescopes and darkening the room, a dim yellow line will be observed, due to the presence of

sodium compounds in the atmosphere. This may be expected in all spectra.

For convenience, it is customary to regulate the scale so that the left-hand margin of the yellow sodium line will exactly coincide with 50.[1] For analysis a thin paste of the salt is supported by a small loop on a platinum wire and held in the non-luminous flame before the collimator slit.

**Spark Spectra.** — Those solids which are vaporized not by a simple flame, but by an electric spark, include a large majority of the elements and compounds. The spectra of gases are also produced by the electric spark, which can be made by an induction coil or influence machine.

For ordinary analyses, a good apparatus consists of a 3-inch spark coil charged with a storage battery of three or five cells. Primary cells are either too weak or too inconstant. The voltage of the coil can be increased by passing the positive pole through a Leyden jar. A support for the substance to be analyzed, such as is represented by the cut, can be made by fusing the end of a platinum wire 4 cm. long into one end of a small, thin glass tube 1 cm. in diameter, so that the wire will stand free on the inside of the tube about 2 cm. from the closed end. Cut the tube so that the edge of the little cup will stand about 1 mm. above the end of the wire. Draw out another piece of thin tubing to a capillary about the length of the inside wire. A number of these cups should be made and kept ready for use in a test-tube of distilled water.
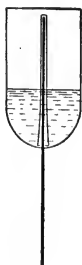
In using this apparatus, first connect the empty cup to the negative pole of the coil by means of a small U-tube filled with mercury. Clamp the positive platinum tipped pole above the cup so that the two poles will be about 1 mm. apart. Close the circuit and make a blank analysis with the spectroscope. Certain bright lines representing the spectra of the gases of the air are often seen. In order to avoid error in subsequent analyses for spark spectra, the presence of these lines should be anticipated. Fill the cup about one-third full of a strong solution of the substance to be analyzed, close the circuit, and examine the spectrum.

**Absorption Spectra.** — Solutions of many substances, both inorganic and organic, and also many gases, give characteristic absorption spectra.

The solvents are various, though water and alcohol are most common. This method not only confirms many line spectra of inorganic compounds, but also affords the only means of spectrum analysis for compounds decomposed by heat. Among the inorganic bodies whose absorption spectra are important to the analyst are the salts of aluminum, iron, cobalt, nickel, and manganese. The most important among organic compounds are the dyes, blood, chlorophyll, etc.

The apparatus necessary for producing absorption spectra is the spectroscope, a white light, and a large test-tube to contain the solution to be examined. First arrange the spectroscope as for flame or spark spectra, and then place the white light about 2 dm. in front of the collimator slit so that a clear continuous spectrum will appear. Interpose between the slit and the white

TABLE VII

Flame Spectra

Spark Spectra

Spark Spectra, continued

Absorption Spectra
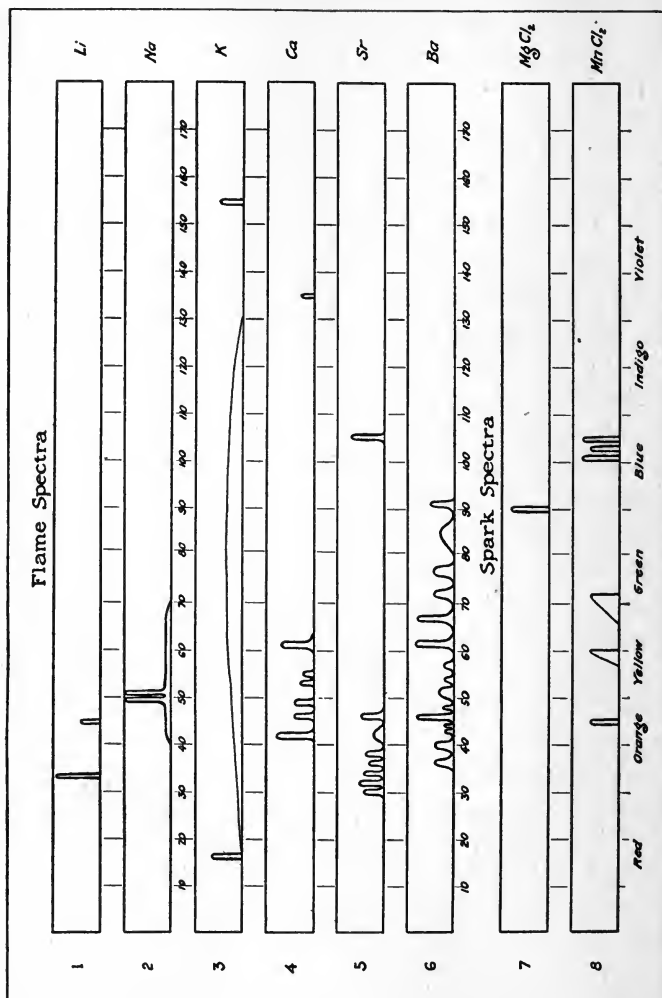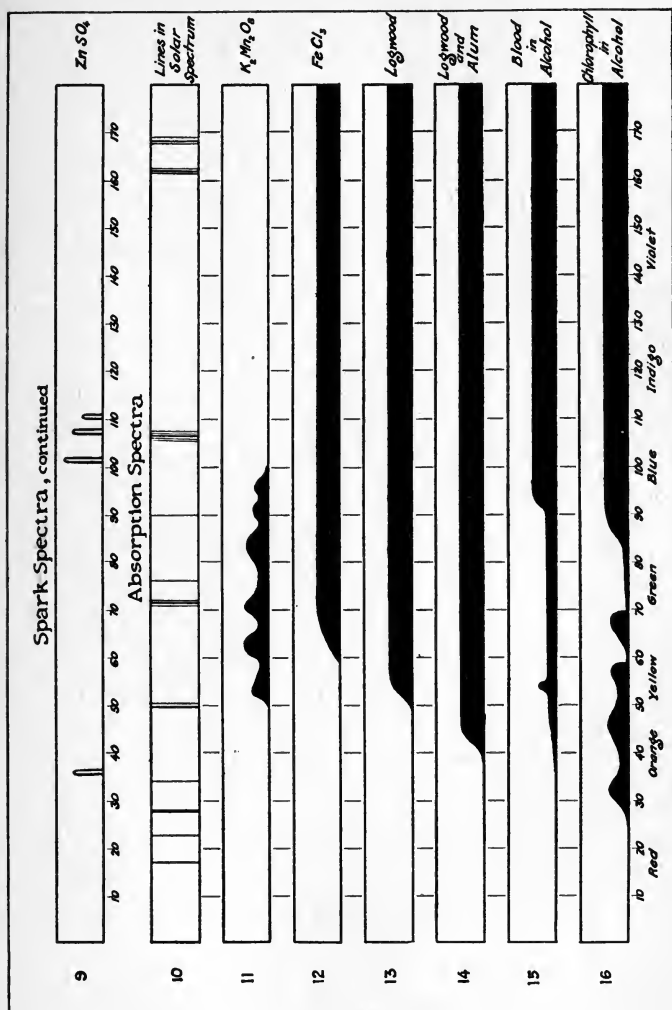
## EXPLANATION OF TABLE VII

Nos. 1, 2, 3, 4, 5, and 6 represent the discontinuous spectra of salts of metals volatile in the flame. The lines and curves in the field of each spectrum indicate the position and distinctness of visible lines. For example, the spectrum of potassium appears on the scale as a strong line between 10 and 20, — more accurately 17, — and another thinner and shorter line between 150 and 160, — more accurately 154. The long curve from 20 to 130 shows that there are many indistinct lines within that area, and the varying heights of the curve indicate the relative distinctness of the lines.

Nos. 7, 8, and 9 represent the discontinuous spectra of salts of metals volatilized by the electric spark. Spark spectra are characterized by the small number of narrow lines and the absence of indistinct lines. No. 10 represents the absorption spectrum of sunlight, showing the so-called Fraunhofer's lines.

Nos. 11, 12, 13, 14, 15, and 16 represent absorption spectra. The shaded parts show the portion of the spectrum absorbed, and the curved margins the relative degrees of absorption.

light the test-tube filled with a dilute solution of the substance. Certain portions of the continuous spectrum will now appear dark.

**Mapping Spectra.** — Two methods have been adopted for recording spectra: —

1. Kirchoff and Bunsen's scale,[1] by which the positions of the lines are recorded on a graduated scale. The conventional practice is to adjust the scale so that the yellow sodium line shall coincide with 50 on the scale. This method is quite simple, and though not so accurate as the other method, it is generally used for chemical analysis.

2. The wave-length method, by which the wave lengths of the colors are calculated from the formula $\lambda = \dfrac{v}{\eta}$, in which $\lambda$, $v$, and $n$, respectively, are wave length, velocity of light, and number of vibrations. The unit is one ten-millionth of a millimeter, called an Ångström.

Professor Rowland of Johns Hopkins University, by means of his improved concave grating spectroscope, has compiled an atlas[2] of a large number of spectra recorded in wave lengths. In this elementary book measurements of wave lengths would not be consistent with the character of the work. Hence the use of Kirchoff and Bunsen's scale is recommended.

The table on pages 58 and 59 includes some illustrations of a method of mapping spectra.

### Experiment 18

(*a*) Examine and map the flame spectra of the following salts: sodium chloride, potassium chloride, lithium chloride, barium chloride, strontium chloride, and calcium chloride.

(*b*) Examine and map the spark spectra of the following salts: magnesium chloride, zinc chloride, manganese chloride, copper chloride, and bismuth chloride.

(*c*) Examine and map the absorption spectra of the following inorganic salts: ferric chloride in water, potassium permanganate in water, chrome alum in water, and cobalt nitrate in alcohol.

(*d*) Examine and map the absorption spectra of alcoholic solutions of blood and fuchsine, and a water solution of logwood.

**Special Method for Aluminum (Vogel).** — Make a solution of extract of logwood by boiling the chips in water. Place a test-tube containing this extract between the spectroscope and a luminous flame. The right end of the spectrum will be absorbed, the extent of absorption depending on the concentration of the logwood. The boundary between the absorbed and unabsorbed parts of the spectrum is made to coincide with a convenient line on the scale. Now add a few drops of a dilute neutral solution of an aluminum salt. This will cause the boundary line to move to the left in proportion to the concentration of the solution. The aluminum salt solution is made neutral by adding to it, drop by drop, a very dilute solution of ammonia, until a slight but permanent precipitate is produced.

Neutral ferric salts give the same reaction, but iron can be tested for in the wet way. In case of a mixture of aluminum and iron salts, the iron can be removed by adding an excess of ammonium sulphocyanate solution and shaking out the ferric sulphocyanate with ether. The colorless aqueous portion is tested for aluminum salts. (See Nos. 13 and 14 on the table.)

**Special Method for Magnesium.** — Make a dilute solution of *alcana* and record its absorption spectrum. Now add a dilute neutral solution of magnesium chloride. The alcana spectrum will be moved to the left in proportion to the concentration of the magnesium-chloride solution.

**Special Method for Manganese.** — Boil the compound with some lead dioxide and a little nitric acid and test for the absorption spectrum of permanganic acid. (See No. 11 on the table.)

**Special Method for Cobalt (Wolff).** — Add ammonium sulphocyanate to the cobalt-chloride solution and shake with alcohol (amyl preferable) and ether. This dissolves the cobaltous sulphocyanate, and the solution gives a characteristic absorption spectrum.

**Special Method for Iodine (Vogel).** — Iodine can be tested for with the apparatus here shown: *a* is the gas flame colored by the iodide; *b* is a hard glass tube held in position over the smaller tube by a spiral copper wire, *c*; *d* is a hard glass test-tube containing at its bottom a mixture, *e*, of copper oxide and an iodide; *f* is a stream of illuminating gas passing through the apparatus and burning at *a*; *g* is the spectroscope; *h* is a gas burner.
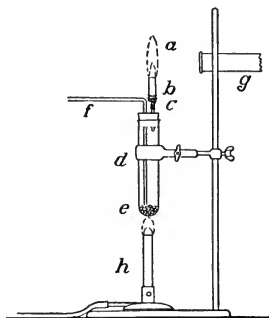


Bromine and chlorine can also be detected in the same manner by using a bromide or a chloride instead of an iodide. The copper iodide, or chloride, or bromide

escapes with the gas and colors the flame green. The spectroscope shows a number of bands, especially in the green part of the spectrum, which are different for iodine, chlorine, and bromine.

# CHAPTER V

## LIST AND PREPARATION OF REAGENTS

It is desirable that the student know not only the chemical nature of reagents, but also their proper dilution. From a careful study of the principles of solution and of mass action, the reason for a knowledge of dilution must be obvious.

In Exp. 4 an illustration is given of the different effects of concentrated and dilute sulphuric acid on zinc.

Furthermore, it is desirable that reagents be so diluted as to give uniform strengths, so that the volume of solution used will be an index of the quantity of reagent employed. Most analysts use an arbitrary system of dilutions that has no special significance, save that it meets the empirical requirements of ordinary analysis.

Reddrop (1890) suggested that dilutions be based on the equivalent weights of the reagents. The equivalent weight of a substance is its molecular weight divided by the number of its replaceable hydrogen atoms, or those which are the equivalents of hydrogen. For example, the equivalent weight of hydrochloric acid is 36.5, obtained by dividing its molecular weight by its number of replaceable hydrogen atoms:

$$36.5 \div 1 = 36.5.$$

Likewise, the equivalent weights of sodium chloride, sodium hydroxide, and silver nitrate are, respectively,

58.5, 40, and 170. The equivalent weight of sulphuric acid is 49, obtained by dividing its molecular weight by its number of replaceable hydrogen atoms:

$$98 \div 2 = 49.$$

The following list gives some equivalent weights:

| | |
|---|---|
| Hydrogen, H . . . . . . . . . . . . | 1. |
| Oxygen, O . . . . . . . . . . . . | 8. |
| Hydrochloric Acid, HCl . . . . . . . | 36.5. |
| Nitric Acid, $HNO_3$ . . . . . . . | 63. |
| Sulphuric Acid, $H_2SO_4$ . . . . . . | 49. |
| Acetic Acid, $HC_2H_3O_2$ . . . . . . | 60. |
| Phosphoric Acid, $H_3PO_4$ . . . . . . | 32.6. |
| Ammonium Chloride, $NH_4Cl$ . . . . . | 53.7. |
| Barium Chloride, $BaCl_2$ . . . . . . | 103.8. |

When equivalent weights are dissolved in equal volumes of water, equal fractional parts of the solutions will be equivalent. A *normal solution* of a substance is one which contains the equivalent weight of that substance, in grams, dissolved in a liter of solution. For example, a normal solution of sodium chloride is its equivalent weight, 58.5 grams, dissolved in sufficient water to produce a liter of solution.

Equal volumes of normal solutions whose solutes react with one another should neutralize each other perfectly, leaving no excess of either reagent, as in the following equation: $AgNO_3 + NaCl = AgCl + NaNO_3.$

#### Experiment 19

Arrange two burettes. Fill the one with a normal solution of sulphuric acid, and the other with a normal solution of sodium hydroxide. Into a beaker or flask measure out 20 c.c. of the

alkali and add about 1 c.c. litmus solution. Now add the acid from the burette, drop by drop, stirring or shaking constantly, till the blue color changes to red. Compare the volumes of the two solutions used.

NOTE. — The normal solutions in this experiment should be prepared by the instructor.

Theoretically, solutions of all reagents should be of equivalent strengths; but it has not been found practical to give all of them these values because of their lack of uniform solubilities. It is convenient to adopt the normal solution as a standard and to express all dilutions as multiples or fractions of normal.

The letter **N** is used to denote a normal solution, and all variations from normal are expressed in terms of **N**. For example, the best dilution for sulphuric acid is about five times its normal strength, expressed thus: $5\,\mathbf{N}\,H_2SO_4$, or $5\,\mathbf{N}$ solution; and the best dilution for silver nitrate is about one-fifth its normal strength, expressed thus: $\dfrac{\mathbf{N}}{5}\,AgNO_3$, or $\dfrac{\mathbf{N}}{5}$ solution.

It is sufficient for the purposes of qualitative analysis if the strength of the reagents be approximately known, and it will be understood that the strengths given below are only approximate.

### LIST OF REAGENTS

**Solutions.** — 1. *Acetic Acid*, $HC_2H_3O_2 + Aq.$ 1 volume 80% acid to 2 volumes water $= 5\,\mathbf{N}$ solution.

2. *Concentrated Hydrochloric Acid*, HCl. Sp. gr. 1.20 $=$ 11 **N** solution.

3. *Dilute Hydrochloric Acid*, HCl $+$ Aq. 1 volume concentrated acid to 3 volumes water $= 5\,\mathbf{N}$ solution.

**4.** *Hydrosulphuric Acid Gas,* $H_2S$. For generating the gas Kipp's apparatus is generally used.[1] The generator should be kept in a hood with a good draught. The materials used in the generator are lumps of ferrous sulphide, FeS, and dilute hydrochloric or sulphuric acid. Often when the acid seems exhausted it will renew its activity if it is removed from the generator, and the lumps of ferrous sulphide thoroughly washed with water.

**5.** *Hydrosulphuric Acid Solution,* $H_2S + Aq$. The gas is passed into cold water to saturation. The solution of the gas should be kept in the dark or in bottles of deeply colored glass, as sunlight decomposes the acid with separation of sulphur.

**6.** *Concentrated Nitric Acid,* $HNO_3$. Sp. gr. $1.42 = 16$ **N** solution.

**7.** *Dilute Nitric Acid,* $HNO_3 + Aq$. 5 volumes concentrated acid to 11 volumes water $= 5$ **N** solution.

**8.** *Concentrated Sulphuric Acid,* $H_2SO_4$. Sp. gr. $1.84 = 36$ **N** solution.

**9.** *Dilute Sulphuric Acid,* $H_2SO_4 \cdot 2 H_2O + Aq$. 1 volume concentrated acid to 6 volumes water $= 5$ **N** solution. In diluting the concentrated acid, it should be added to the water very slowly, in a large porcelain dish, and allowed to cool before using.

**10.** *Tartaric Acid,* $H_2C_4H_4O_6 + Aq$. 1 part crystals to 13 parts water $=$ **N** solution. The acid decomposes in solution and should be prepared fresh each time.

**11.** *Aqua Regia,* $HCl + HNO_3$. 1 volume concentrated nitric to 3 volumes concentrated hydrochloric acid. This proportion is sometimes varied for specific purposes. As a solvent, just enough of the reagent should be used to dissolve the substance completely. A large excess must be avoided, since if allowed to remain it decomposes other reagents, while if evaporated certain volatile chlorides,

*e.g.,* arsenic and mercuric chlorides, are liable to be lost. Prepare aqua regia fresh each time it is needed.

**12.** *Ammonium Chloride,* $NH_4Cl + Aq.$ Use 1 part crystals to 4 parts water, and allow it to rise to the natural temperature; then dilute with 1 part water $= 5$ **N** solution.

**13.** *Ammonium Carbonate,* $(NH_4)_2CO_3 + Aq + NH_4OH.$ 4 parts solid ammonium carbonate dissolved in 7 parts 5 **N** $NH_4OH$; then dilute with 14 parts water $= 5$ **N** solution.

**14.** *Ammonium "Sesqui" Carbonate.* Dissolve 1 part solid $(NH_4)_2CO_3$ in 9 parts water and add for each 10 c.c. of the liquid 5 drops of strong ammonia (Hager). Prepare fresh each time.

**15.** *Concentrated Ammonium Hydroxide,* $NH_4OH + Aq.$ Sp. gr. $0.90 = 9$ **N** solution.

**16.** *Dilute Ammonium Hydroxide,* $NH_4OH + Aq.$ 2 volumes concentrated ammonia water (sp. gr. 0.90) to 5 volumes water $= 5$ **N** solution. Both concentrated and dilute ammonia attack glass vessels ; and if white flakes appear in the clear solutions, they should be filtered out before use.

**17.** *Ammonium Oxalate,* $(NH_4)_2C_2O_4 \cdot H_2O + Aq.$ 1 part solid crystals to 25 parts water $= \dfrac{N}{2}$ solution.

**18.** *Ammonium Sulphide,* $(NH_4)_2S + Aq + NH_4OH.$ Saturate 3 parts 5 **N** ammonia with hydrogen sulphide gas, and then add 2 parts 5 **N** ammonia solution. This reagent should be made frequently, as it decomposes on standing.

**19.** *Yellow Ammonium Sulphide,* $(NH_4)_2Sx + Aq + NH_4$ OH. Digest a solution of $(NH_4)_2S$ with a little powdered roll sulphur. An excess of sulphur must be avoided, as it produces the red solution containing higher sulphides.

**20.** *Barium Chloride,* $BaCl_2 \cdot 2H_2O + Aq.$ 1 part solid crystals dissolved in 10 parts water $=$ **N** solution.

**21.** *Bromine*, Br.   Should be kept in a dark, glass-stoppered bottle.

**22.** *Dilute Bromine*, Br + Aq.   Make a saturated solution by shaking an excess of bromine in water $= \dfrac{N}{2}$ solution.   Stronger solutions of bromine can be made by adding potassium bromide to the water solution.

**23.** *Calcium Hydroxide* (*lime water*),  $Ca(OH)_2 +$ Aq. Saturate freshly boiled distilled water by shaking an excess of freshly slaked lime in it, and allowing the excess of lime to settle.   Filtrate $= \dfrac{N}{20}$ solution.

**24.** *Chlorine Water*,  Cl + Aq.   Saturate cold water with chlorine gas $= \dfrac{N}{5}$ solution.   Should be kept in the dark and in brown bottle.

**25.** *Cobalt Nitrate*, $Co(NO_3)_2 \cdot 6\,H_2O +$ Aq.   1 part solid crystals to 7 parts water $=$ **N** solution.

**26.** *Ferric Chloride*, $FeCl_3 +$ Aq.   1 part solid salt to 20 parts water $=$ **N** solution.

**27.** *Ferrous Sulphate*, $FeSO_4 \cdot 7\,H_2O +$ Aq.   1 part solid crystals to 7 parts water $=$ **N** solution.   It is best to prepare this solution fresh, when needed.

**28.** *Lead Acetate*,  $Pb(C_2H_3O_2)_2 \cdot 3\,H_2O +$ Aq.   4 parts solid to 21 parts water $=$ **N** solution.

**29.** *Magnesium Sulphate*, $MgSO_4 \cdot 7\,H_2O +$ Aq.   1 part crystals to 8 parts water $=$ **N** solution.

**30.** *Magnesia Mixture*, $MgCl_2 + NH_4Cl + NH_4OH +$ Aq. Dissolve 6 grams magnesium chloride crystals and 165 grams ammonium chloride in 300 c.c. water; then add 300 c.c. 5 **N** ammonia solution; and dilute to 1 liter $= \dfrac{N}{5}$ solution.

**31.** *Mercuric Chloride*, $HgCl_2 +$ Aq.   1 part solid salt to 37 parts water $= \dfrac{N}{5}$ solution.

**32.** *Hydrochlorplatinic Acid*, $H_2PtCl_6 \cdot 6H_2O + Aq$. **1** part solid salt to **12** parts water $= \mathbf{N}$ solution. The solution can also be prepared by dissolving 0.30 gr. platinum foil in aqua regia, evaporating to dryness, and redissolving in **10** c.c. **5 N** HCl.

**33.** *Potassium Chromate*, $K_2CrO_4 + Aq$. **1** part solid salt to **10** parts water $= \mathbf{N}$ solution.

**34.** *Potassium Cyanide*, $KCN + Aq$. **1** part solid salt to **15** parts water $= \mathbf{N}$ solution. Prepare fresh for each experiment.

**35.** *Potassium Ferricyanide*, $K_3Fe(CN)_6 \cdot 3H_2O + Aq$. **1** part solid salts to **9** parts water $= \mathbf{N}$ solution.

**36.** *Potassium Ferrocyanide*, $K_4Fe(CN)_6 \cdot 3H_2O + Aq$. **1** part solid salt to **10** parts water $= \mathbf{N}$ solution.

**37.** *Potassium Hydroxide*, $KOH + Aq$. **1** part solid caustic potash to **3.5** parts water $= \mathbf{5\,N}$ solution.

**38.** *Potassium Sulphocyanate*, $KCNS + Aq$. **1** part solid salt to **10** parts water $= \mathbf{N}$ solution.

**39.** *Silver Nitrate*, $AgNO_3 + Aq$. **1** part solid salt to **30** parts water $= \dfrac{\mathbf{N}}{5}$ solution.

**40.** *Sodium Acetate*, $NaC_2H_3O_2 \cdot 3H_2O + Aq$. **1** part solid salt to **8** parts water $= \mathbf{N}$ solution.

**41.** *Sodium Carbonate*, $Na_2CO_3 \cdot 1\,OH_2O + Aq$. **1** part solid crystals to **7** parts water $= \mathbf{N}$ solution.

**42.** *Sodium Hydroxide*, $NaOH + Aq$. **1** part solid to **5** parts water $= \mathbf{5\,N}$ solution. First dissolve the solid base in a little water, allow to cool, and then dilute to the required volume.

**43.** *Sodium Phosphate*, $HNa_2PO_4 \cdot 12H_2O + Aq$. **1** part solid crystals to **8** parts water $= \mathbf{N}$ solution.

**44.** *Stannous Chloride*, $SnCl_2 \cdot 2H_2O + Aq$. Dissolve **3** parts solid salt in **3** parts **5 N** hydrochloric-acid solution, and dilute with **20** parts water $= \mathbf{N}$ solution. Pieces of

granulated tin should be kept in the solution.   **An excel-**
lent quality of solid stannous chloride can be made by
heating granulated tin with repeated small quantities of
concentrated HCl, added at intervals whenever ebullition
ceases.   When all the tin is dissolved, evaporate to dry-
ness on the water bath.

**Solvents.** — 45. *Alcohol,* $C_2H_5OH$, 95 per cent.

46. *Carbon Disulphide,* $CS_2$.

47. *Ether,* $(C_2H_5)_2O$, commercial.

48. *Ether-Alcohol,* 1 volume absolute ether to 1 volume
absolute alcohol.

49. *Petroleum Ether.*

50. *Water,* distilled.

**Dry Reagents.** — 51. *Ammonium Chloride,* $NH_4Cl$.

52. *Ammonium Carbonate,* $(NH_4)_2CO_3$.

53. *Cobalt Nitrate,* $Co(NO_3)_2 \cdot 6H_2O$.

54. *Lead Peroxide,* $PbO_2$.

55. *Manganese Peroxide,* $MnO_2$.

56. *Microcosmic Salt,* $HNa(NH_4)PO_4 \cdot 8H_2O$.

57. *Potassium Carbonate,* $K_2CO_3$, anhydrous.

58. *Potassium Cyanide,* $KCN$.

59. *Potassium Disulphate,* $HKSO_4$.

60. *Potassium Nitrate,* $KNO_3$.

61. *Potassium Nitrite,* $KNO_2$.

62. *Sodium Carbonate,* $Na_2CO_3$, anhydrous.

63. *Sodium Tetraborate (borax),* $Na_2B_4O_7 \cdot 10H_2O$.

64. *Sodium Peroxide,* $Na_2O_2$.

# CHAPTER VI

## SYSTEMS OF ANALYTICAL EXAMINATION

**Analysis by the Dry Way.** — The chief operations in analysis by this system are the observations of (a) Oxidation and Reduction, and (b) Flame Coloration.

(a) Oxidation and reduction have been explained under ignition operations. These include fusion in crucibles, closed tube reductions, oxidation and reduction with fluxes on a platinum wire, and reduction on charcoal with and without fluxes.

(b) Flame colorations have been explained under simple flame colorations and spectroscopy.

Though these operations are indispensable to the analyst, they do not constitute an independent system, but are only used for preliminary and confirmatory observations.

**Analysis by the Wet Way.** — Solution is the basis of this system of analysis. Advantage is taken of the following facts: —

(a) The metallic ions of most compounds behave alike towards certain reagents, regardless of the acid radicals which may be present. For example, all soluble silver salts will give insoluble silver chloride with all soluble chlorides.

(b) Differences of solubility of similar compounds of different metals may be utilized in separating them into

groups. For example, silver, lead, and copper sulphides are insoluble in acidified solutions, while some other sulphides, *e.g.*, those of zinc and barium, are soluble under like conditions. Silver and lead chlorides are insoluble, and copper chloride is soluble in acidified solutions. Such differences of solubility afford an easy means of separating and detecting these metals.

(*c*) Physical characteristics, color, odor, etc., are used for detecting individual substances. For example, the soluble salts of both cadmium and copper are precipitated by hydrogen sulphide; but as the one sulphide is a bright yellow and the other black, the two can be distinguished.

(*d*) The principles of the periodic law of elements are in part regarded in analytical chemistry. The periodic groups — sodium, potassium, lithium; barium, strontium, calcium; chlorine, bromine, and iodine — are also utilized as analytical groups.

An ideal natural system of classification would have analytical groups to coincide with periodic groups; but in this respect analytical classification is somewhat artificial, and depends more upon differences in degree of the physical property of solubility than on chemical properties. For example, magnesium, zinc, and cadmium belong to the same periodic group, but, by reason of the differences in the solubilities of their sulphides, the three metals are placed in three separate analytical groups.

By (*a*) all salts require two analyses: first, for metals; and, second, for the acid radicals. By (*b*) and (*c*) the metals are divided into groups depending on

the insolubility of their chlorides, sulphides, hydroxides, and carbonates.

There are six groups of metals : —

Group I, whose chlorides are insoluble in aqueous solution ;

Group II, whose sulphides are insoluble in acidified (HCl) solution ;

Group III, whose hydroxides are insoluble in alkaline ($NH_4OH$) solution ;

Group IV, whose sulphides are insoluble in alkaline ($NH_4OH$) solution ;

Group V, whose carbonates are insoluble in alkaline ($NH_4OH$) solution ;

Group VI, which has no group characteristic.

The group reagent would be for : —

Group I, a soluble chloride (HCl) ;

Group II, a soluble acidified sulphide ($H_2S$ with HCl) ;

Group III, a soluble alkali ($NH_4OH$ with $NH_4Cl$) ;

Group IV, a soluble alkaline sulphide [$(NH_4)_2S$ with $NH_4OH$ and $NH_4Cl$] ;

Group V, a soluble alkaline carbonate [$(NH_4)_2CO_3$ with $NH_4OH$ and $NH_4Cl$] ;

Group VI, no group reagent.

By (*b*) and (*d*) the acids are also divided into groups depending on the insolubility of their barium and silver salts, hence the three groups : —

Group I, whose barium salts are insoluble in aqueous solution ;

Group II, whose silver salts are insoluble in dilute acid solution ;

Group III, which has no group reagent.

By (*b*) and (*c*) the individual metals and acid radicals included in the groups are separated and distinguished. For example, silver, lead, and mercury (mercurous) chlorides are thrown down by hydrochloric acid as white precipitates.

The separation is accomplished by observing facts like these: Lead chloride is soluble in hot water; silver and mercurous chlorides are not. Silver chloride is soluble in ammonia; white mercurous chloride is not soluble, but is blackened by that reagent. Thus, both the differences of solubility and color are used for separating and detecting metals.

# PART II—REACTIONS AND SEPARATIONS[1]

## CHAPTER VII

### METALS OF GROUP I: SILVER, MERCURY (MERCUROUS SALTS, Hg′), AND LEAD

CHARACTERISTIC: **Insolubility of the chlorides in cold water or dilute HCl.**

GROUP REAGENT: **Dilute hydrochloric acid.**

#### REACTIONS

### Silver (salt for study, silver nitrate, AgNO₃).

**1. HCl** precipitates white silver chloride, AgCl, darkening in the sunlight; insoluble in $HNO_3$;[2] soluble in $NH_4OH$.

The soluble compound formed by adding $NH_4OH$ to AgCl is variously regarded as $2\,AgCl \cdot 3\,NH_3$, $AgCl \cdot 2\,NH_3$, and $AgCl \cdot 3\,NH_3$, though the preponderance of authority favors $2\,AgCl \cdot 3\,NH_3$. $NH_4OH$ also unites with many other salts, especially those of mercury, copper, and cobalt (which see).

---

[1] The student is urged again to be methodical and thoughtful in his laboratory exercises, especially in the execution of the reactions and separations in this part of the book.

For convenience and economy of space, the reagents hereafter referred to are generally expressed by molecular formulas,—not by names; but the student should not on this account contract the bad habit of calling chemical substances by their formulas. For illustration, "hydrogen sulphide"—not "$H_2S$"—should be the spoken name for the compound.

Some seem to be derivatives of ammonia, and others of the quasi-metal, ammonium. (See Remsen's *Inorganic Chemistry*, p. 274.)

The theory that these substances are chemical compounds — not "molecular additions" — is in harmony with their conduct. In all of them there has been a shifting of the atoms of the metallic salts and ammonia to form more complex ions, thus producing radical changes in their solubilities and chemical conduct.

2. **$H_2S$** precipitates black silver sulphide, $Ag_2S$, soluble in boiling $HNO_3$.

3. **$NH_4OH$**[1] precipitates brown silver oxide, $Ag_2O$, soluble in excess of reagent.

4. **NaOH** gives similar results to $NH_4OH$, except that the precipitate is not soluble in excess of reagent.

5. **$K_2CrO_4$** precipitates dark-red silver chromate, $Ag_2CrO_4$, soluble in hot $HNO_3$ and in $NH_4OH$.

6. **Metallic copper** deposits metallic silver on its surface.

7. **Reducing flame** on charcoal with $Na_2CO_3$, or, better, with the fusion mixture of $Na_2CO_3$ and $K_2CO_3$, gives a metallic silver bead.

$Na_2CO_3$ acts partly as a flux, thus making possible the ionization of $AgNO_3$ and $Na_2CO_3$, and partly as an active chemical agent. The following reactions occur here : —

$$2\,AgNO_3 + Na_2CO_3 = Ag_2CO_3 + 2\,NaNO_3 ;$$
$$Ag_2CO_3 + heat = Ag_2O + CO_2 ;$$
$$2\,Ag_2O + C = 4\,Ag + CO_2.$$
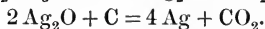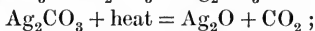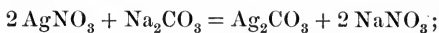
## Mercurous Mercury, Hg′ (salt for study, mercurous nitrate, $Hg_2(NO_3)_2$).

1. **HCl** precipitates white mercurous chloride or calomel, $Hg_2Cl_2$, soluble in hot $HNO_3$ ; insoluble in $NH_4OH$, forming a black substance.

· The black insoluble substance is amido-mercurous chloride ("black precipitate"), $NH_2Hg'_2Cl$, or possibly a mixture of $NH_2Hg''Cl$ ("white precipitate") and metallic mercury:—

$$Hg_2Cl_2 + 2 NH_4OH = NH_2HgCl + Hg + NH_4Cl + 2 H_2O.$$

**2. $H_2S$** precipitates a black mixture of mercuric sulphide[1] and mercury, $HgS + Hg$, soluble in aqua regia.

The action of aqua regia depends on the following:—

$$3 HCl + HNO_3 = Cl_2 + NOCl + 2 H_2O ;$$
$$2 HgS + Cl_2 + 2 NOCl = 2 HgCl_2 + 2 NO + 2 S.$$
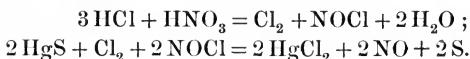
**3. $NH_4OH$** produces a black precipitate[2] of unknown composition, insoluble in excess of reagent.

**4. NaOH** produces a black precipitate of mercurous oxide, $Hg_2O$, insoluble in excess of reagent.

**5. $SnCl_2$** precipitates gray metallic mercury, distinct when boiled with HCl.

The action of $SnCl_2$ on mercurous salts depends on the tendency of stannous salts to oxidize to the stannic condition, on which account they act as energetic reducing reagents. Mercurous salts are reduced to metallic mercury, and mercuric salts are first reduced to mercurous and then to metallic mercury:—

$$Hg_2Cl_2 + SnCl_2 = 2 Hg + SnCl_4 ;$$
$$2 HgCl_2 + SnCl_2 = Hg_2Cl_2 + SnCl_4 ;$$
$$Hg_2Cl_2 + SnCl_2 = 2 Hg + SnCl_4.$$
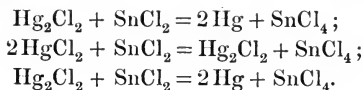
**6. KI** precipitates green mercurous iodide, $Hg_2I_2$, soluble in acids.

**7. Metallic copper** deposits metallic mercury, distinct when polished.

**8. Heating** in a closed tube, with fusion mixture, deposits globules of metallic mercury on the sides of the tube.

## Lead (salt for study, lead nitrate, Pb $(NO_3)_2$).

1. **HCl** precipitates white lead chloride, $PbCl_2$, soluble in boiling water, and in concentrated HCl.

2. **$H_2S$** precipitates black lead sulphide, PbS, soluble in hot $HNO_3$.

3. **$NH_4OH$** and **NaOH** precipitate white lead hydroxide, $Pb(OH)_2$, soluble in excess of NaOH, forming the sodium salt $Na_2PbO_2$. If $NH_4OH$ is used for precipitation, and NaOH for redissolving the precipitate, the latter should be filtered and washed before adding the NaOH. This is necessary in order to eliminate ammonium salts which prevent the formation of $Na_2PbO_2$.

4. **$H_2SO_4$** precipitates white lead sulphate, $PbSO_4$, soluble in hot NaOH and in $NH_4C_2H_3O_2$.

5. **$K_2CrO_4$** precipitates yellow lead chromate, $PbCrO_4$, soluble in NaOH, forming $Na_2PbO_2$.

6. **KI** precipitates yellow lead iodide, $PbI_2$,[1] soluble in hot water and in excess of KI.

7. **Metallic zinc** deposits metallic lead.

8. **Reducing flame** on charcoal, with fusion mixture, precipitates metallic lead.

### PROCESS OF SEPARATION

The separation of the members of this group is based upon the fact that $PbCl_2$ is soluble in hot water, and that AgCl is soluble in $NH_4OH$. The process of separation is as follows: —

Add cold dilute HCl so long as the white precipitate continues to be formed; then add about ten drops

in excess. Filter and wash[1] with cold water[2] (ice water is preferable). Filtrate (*a*) may contain members of all the subsequent groups ; residue (*a*) may consist of $PbCl_2$, $AgCl$, and $Hg_2Cl_2$. Pour boiling water on the residue in the filter[3] and test the filtrate (*b*) with $K_2CrO_4$ for lead, and, if present, continue the washing with hot water till all traces of it disappear. Add warm $NH_4OH$ to the residue (*b*) on the filter and test the filtrate (*c*) for silver[4] by neutralizing with $HNO_3$. Precipitation of $AgCl$ confirms the presence of silver. If a black residue (*c*) is left after adding $NH_4OH$, mercury is probably present. Confirm by dissolving in a little aqua regia, evaporating excess of chlorine and acids, and adding $SnCl_2$.

A certain amount of care must be observed on adding HCl, since dilute HCl often precipitates certain members of the next group (BiOCl and SbOCl). This source of error can be removed by adding a sufficient excess of HCl, which redissolves the BiOCl and SbOCl.

On the other hand, too great an excess of HCl interferes with the action of the next group reagent ($H_2S$); and, furthermore, it may redissolve the chlorides of Group I.

# CHAPTER VIII

**METALS OF GROUP II: MERCURY (MERCURIC SALTS, Hg″), LEAD, BISMUTH, COPPER, CADMIUM, ARSENIC (ARSENIOUS, As‴, AND ARSENIC, As$^V$, SALTS), ANTIMONY, AND TIN**

CHARACTERISTIC: **Insolubility of the sulphides in dilute HCl.**
GROUP REAGENT: **Hydrogen sulphide in the presence of hydrochloric acid.**

## REACTIONS

### Mercuric Mercury, Hg″ (salt for study, mercuric chloride, $HgCl_2$).

**1. $H_2S$** precipitates black mercuric sulphide, HgS, soluble in aqua regia; insoluble in yellow $(NH_4)_2S_x$ and in hot $HNO_3$.

When $H_2S$ is first added, a white precipitate is obtained which is the salt, $HgCl_2 \cdot 2\,HgS$. On adding more $H_2S$, it becomes orange, brown, and then black. If insufficient $H_2S$ is added, it remains orange and is often mistaken for $Sb_2S_3$ (which see).

**2. $NH_4OH$** precipitates "white precipitate," $NH_2 \cdot HgCl$, soluble in acids.

**3. NaOH** precipitates yellow mercuric oxide, HgO, soluble in acids.

**4. $SnCl_2$** precipitates white $Hg_2Cl_2$, changing to gray metallic mercury by addition of an excess of reagent. Boiling with a little HCl causes metallic globules to form.

**5. KI** precipitates scarlet mercuric iodide, $HgI_2$,[1] soluble in excess of reagent, forming $2KI \cdot HgI_2$.

6. **Metallic copper** deposits metallic mercury.

7. **Heating** in a closed tube with fusion mixture causes separation of metallic mercury.

### Lead. (See reactions for lead under Group I.)

Lead, when present in a mixture, is often found in Group II, because $PbCl_2$ is somewhat soluble in acidified aqueous solutions, and is brought over with the filtrate from Group I.

### Bismuth (salt for study, bismuth nitrate, $Bi(NO_3)_3$).

1. $H_2S$ precipitates black bismuth sulphide, $Bi_2S_3$, soluble in boiling $HNO_3$; insoluble in $(NH_4)_2S_x$. The precipitation is hastened by dilution.

2. $NH_4OH$ and **NaOH** precipitate white basic bismuth hydroxide, $(BiO)OH$, soluble in acids. If made alkaline again with NaOH, and $SnCl_2$ is added, black bismuth monoxide, BiO, will be formed.

3. **Water** added in large excess precipitates white bismuth oxynitrate, $(BiO)NO_3$, soluble in acids. Addition of NaCl hastens the precipitation by the formation of the less soluble $(BiO)Cl$ by double decomposition.

In this experiment, both water and $HNO_3$ (a constituent of $Bi(NO_3)_3$) endeavor to react with bismuth, the one to form insoluble basic $(BiO)NO_3$ and the other to maintain the soluble nitrate $Bi(NO_3)_3$. $HNO_3$ is far better ionized than water, and with a degree of equality in the contest it would maintain the salt $Bi(NO_3)_3$; but the large excess of water so handicaps the acid that it yields to mass action. In this hydrolytic action the positive ion, Bi, is changed to another positive ion, BiO (bismuthyl).

4. **Metallic iron or zinc** deposits metallic bismuth.

5. **Reducing flame** on charcoal with fusion mixture gives a brittle bead of metallic bismuth. The border of the pit becomes coated with yellow bismuth trioxide, $Bi_2O_3$.

### Copper (salt for study, copper sulphate, $CuSO_4$).

1. $H_2S$ precipitates black copper sulphide, $CuS$, soluble in $HNO_3$ and $KCN$; almost insoluble in $(NH_4)_2S_x$; insoluble in dilute $H_2SO_4$ and yellow $Na_2S_x$.

2. $NH_4OH$ precipitates a greenish basic cupric salt, probably $CuSO_4 \cdot CuO$, soluble in excess of reagent, forming a blue cuprammonium compound.[1]

3. **NaOH** precipitates blue copper hydroxide, $Cu(OH)_2$, darkening on boiling and giving $3CuO \cdot H_2O$.

4. **Metallic iron or zinc** deposits metallic copper.

5. **Reducing flame** on charcoal with fusion mixture gives metallic copper. The finely divided copper is easily detected after the reduction by triturating the fused mass in a small mortar and then washing off the charcoal and dissolved salts.

6. **KCN** precipitates greenish cupric cyanide, $Cu(CN)_2$, soluble in excess of reagent, forming the salt $CuCN \cdot 3KCN$ or $K_3Cu(CN)_4$. This salt is not reprecipitated by $H_2S$. This is the reverse of Reaction 1.

7. $K_4Fe(CN)_6$ precipitates brown cupric ferrocyanide, $Cu_2Fe(CN)_6$, insoluble in dilute acids.

### CHEMISTRY OF CYANOGEN COMPOUNDS

As cyanogen compounds are important in many analytical reactions, it is necessary to consider their behavior and constitution at some length.

Cyanogen, CN, is much like the halogens, in both the constitution and behavior of its acids and salts. The cyanogen analogues of HCl, KCl, HClO, KClO, etc., are, respectively, HCN, KCN, HCNO, KCNO, etc.

The cyanides of the more basic metals, the alkali and alkali-earth metals, are soluble and easily decomposed by acids, while those of the less basic heavy metals are less soluble and more stable in the presence of acids. Though the cyanides of the strong basic metals are easily decomposed by acids, they are not readily dissociated by heat and can be fused without decomposition. The reverse is true of the cyanides of the weak basic metals. Many insoluble cyanides unite with soluble cyanides to form so-called "double cyanides" : —

$CuCN + 3KCN = CuCN \cdot 3KCN$ or $K_3Cu(CN)_4$, potassium cuprous cyanide ;

$Fe(CN)_2 + 4KCN = Fe(CN)_2 \cdot 4KCN$ or $K_4Fe(CN)_6$, potassium ferrous cyanide ;

$Fe(CN)_3 + 3KCN = Fe(CN)_3 \cdot 3KCN$ or $K_3Fe(CN)_6$, potassium ferric cyanide;

$Co(CN)_2 + 4KCN = Co(CN)_2 \cdot 4KCN$ or $K_4Co(CN)_6$, potassium cobaltous cyanide.

The behavior, with reagents, of the solutions of many of these combined salts indicates that they are not mixtures of binary cyanides but salts of ternary acids whose acid radicals are cyanides of various metals. For convenience the term *metallo-cyanide* is applied to this class of salts.

Copper is usually precipitated as CuS by $H_2S$ in acid solution, but this reaction does not occur if $K_3Cu(CN)_4$ is treated with $H_2S$. This seems to indicate that there are no free Cu ions in a solution of $K_3Cu(CN)_4$. Potassium cyanide reacting with $H_2S$ liberates hydrocyanic acid, HCN, but when $K_3Cu(CN)_4$ is treated with $H_2S$, HCN is not evolved. Both examples show that the two constituents of the salt, CuCN and KCN, are so strongly united as to destroy the identity of each, and that $K_3Cu(CN)_4$ is the preferable formula.

This view is important in analytical chemistry, as it interprets the behavior of several substances similar to $K_3Cu(CN)_4$.

The metallo-cyanides occurring in analytical chemistry may be considered under three classes : —

1. Metallo-cyanides decomposed by hydrogen sulphide : —

$$K_2Cd(CN)_4 + 2H_2S = CdS + K_2S + 4HCN;$$
$$K_2Hg(CN)_4 + 2H_2S = HgS + K_2S + 4HCN, \text{ etc.}$$
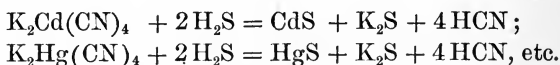
This class is important in the separation of copper and cadmium in Group II for metals.

2. Metallo-cyanides decomposed by dilute mineral acids : —

$$K_3Cu(CN)_4 + 3HCl = CuCN + 3KCl + 3HCN;$$
$$K_2Ni(CN)_4 + 2HCl = Ni(CN)_2 + 2KCl + 2HCN;$$
$$K_4Co(CN)_6 + 4HCl = Co(CN)_2 + 4KCl + 4HCN, \text{ etc.}$$
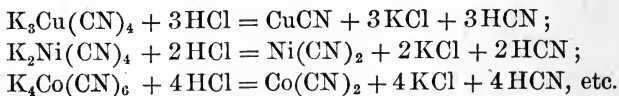
The reaction of $K_4Co(CN)_6$ is merely temporary, and the actual product is $K_3Co(CN)_6$, showing that the cobaltous salt is oxidized to the corresponding cobaltic salt. The nickelous salt is not oxidized to the nickelic salt. This is further illustrated in the oxidation of $K_2Ni(CN)_4$ and $K_4Co(CN)_6$ by a hypobromite : —

$$2 \, K_2Ni(CN)_4 + NaBrO + 5 \, H_2O = 2 \, Ni(OH)_3 + NaBr$$
$$+ \, 4 \, KCN + 4 \, HCN ;$$
$$2 \, K_4Co(CN)_6 + NaBrO + H_2O = 2 \, K_3Co(CN)_6 + NaBr$$
$$+ \, 2 \, KOH.$$
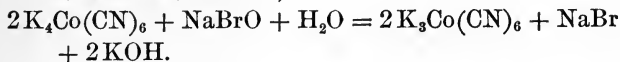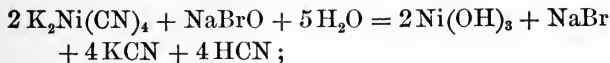
This class is important in the separation of nickel and cobalt in Group IV for metals.

3. Metallo-cyanides not decomposed by dilute mineral acids.

The members of this class are stable chemical compounds and are not decomposed except by drastic treatment. They give a clearer insight into the constitution of the metallo-cyanides. The most important are the three reagents, potassium ferrocyanide, $K_4Fe(CN)_6$, potassium ferricyanide, $K_3Fe(CN)_6$, and potassium sulphocyanate, $KCNS$.[1] They react with many compounds and, for the most part, form colored metallo-cyanides : —

$$2CuSO_4 + K_4Fe(CN)_6 \quad = 2 \, K_2SO_4 + Cu_2Fe(CN)_6 ;$$
$$4FeCl_3 + 3 \, K_4Fe(CN)_6 = 12 \, KCl + Fe_4(Fe(CN)_6)_3 ;$$
$$3FeSO_4 + 2 \, K_3Fe(CN)_6 = 3 \, K_2SO_4 + Fe_3(Fe(CN)_6)_2 ;$$
$$FeCl_3 + 3 \, KCNS \quad\quad = 3 \, KCl + Fe(CNS)_3.$$
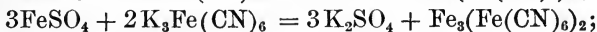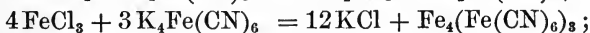
This class is important in the detection of copper and ferrous and ferric iron.

## Cadmium (salt for study, cadmium nitrate, $Cd(NO_3)_2$.

1. $H_2S$ precipitates yellow cadmium sulphide, $CdS$, very soluble in boiling acids; insoluble in cold dilute acids, $(NH_4)_2S_x$, and $KCN$.

2. $NH_4OH$ precipitates white cadmium hydroxide, $Cd(OH)_2$, soluble in excess of reagent.

3. $NaOH$ acts like $NH_4OH$, but does not redissolve $Cd(OH)_2$ in excess of reagent.

4. **Metallic zinc** deposits metallic cadmium.

5. **Reducing flame** on charcoal with fusion mixture gives a brown incrustation of cadmium oxide, CdO. The salt is first reduced to metallic cadmium, which, owing to its ready volatility, rises to a stratum of oxygen and is oxidized.

## Arsenious Arsenic, As''' (salt for study, sodium arsenite, $Na_3AsO_3$).

1. **$H_2S$** precipitates from acidified solutions, yellow arsenious sulphide, $As_2S_3$, soluble in $(NH_4)_2S_x, (NH_4)_2CO_3$, and aqua regia; insoluble in concentrated boiling HCl.

2. **$AgNO_3$** precipitates from very weak ammoniated solutions, yellow silver arsenite, $Ag_3AsO_3$, soluble in excess of $NH_4OH$ and $HNO_3$.

3. **$CuSO_4$** precipitates from ammoniated solutions, Scheele's green, $HCuAsO_3$, soluble in excess of $NH_4OH$.

4. **Heating** in a closed tube with $Na_2CO_3$ and KCN deposits a mirror of metallic arsenic on the cold part of the tube.

5. **Nascent hydrogen** reduces arsenic compounds to arsine, $AsH_3$. If the hydrogen and the $AsH_3$ are passed through a jet tip and kindled, $AsH_3$ will first be oxidized to metallic arsenic and then, on emerging from the flame, will be further oxidized to $As_2O_3$. If $AsH_3$ is passed into a solution of $AgNO_3$, metallic silver and arsenious acid, $H_3AsO_3$, will be produced: —

$$6\,AgNO_3 + AsH_3 + 3\,H_2O = 6\,Ag + 6\,HNO_3 + H_3AsO_3.$$
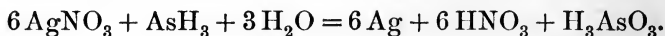
These reactions constitute the principles of —

*Marsh's Test*[1] *for Arsenic.* — Generate hydrogen in a small flask with pieces of pure zinc or magnesium and dilute $H_2SO_4$ or HCl. The flask should have a funnel tube, and the horizontal delivery tube should have a wide, hard glass tube about 2 cm. in diameter and 3 dm. long, drawn to a jet point, and with two constrictions near the middle. When the zinc is put into the flask and all connections made tight, the dilute acid is poured through the funnel tube. After two or three minutes, test the hydrogen by collecting by displacement of water in a test-tube. If it kindles quietly with a blue flame, the jet may now be lighted. To insure safety a cloth should be thrown over the apparatus. Test the reagents and apparatus for arsenic by holding a cold porcelain dish at the top of the flame. If no black spots appear, no arsenic is present.

A concentrated HCl solution of the arsenic compound is poured through the funnel. Arsenic can be detected in four ways : —

(*a*) The hydrogen flame assumes a pale violet color, due to the oxidation of $AsH_3$ to white $As_2O_3$.

(*b*) Black spots of metallic arsenic are deposited on a cold porcelain plate. The plate should not be heated too much, as the arsenic would then be sublimed. The black spots can be removed by a solution of sodium hypochlorite : —

$$10\,NaClO + 4\,As + 6\,H_2O = 10\,NaCl + 4\,H_3AsO_4.$$
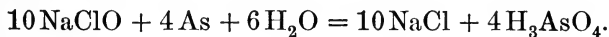
(*c*) If the hard glass tube is heated at one of the contractions, the heat will decompose the passing $AsH_3$

and will cause metallic arsenic to be deposited on the cold part of the tube. When the evolution of hydrogen is completed, detach the tube with the arsenic mirror from the generator and pass $H_2S$ through the slightly warmed tube. The metallic mirror will change to yellow $As_2S_3$.

(d) *Hofmann's Modification.* — Instead of kindling $AsH_3$, pass it through a U-tube containing glass splinters or beads moistened with a solution of lead acetate, in order to counteract any passing HCl or $H_2S$, and then pass the gas into a test-tube containing a solution of $AgNO_3$. When the precipitation is completed, remove the test-tube and add very cautiously a thin stratum of very dilute $NH_4OH$. The junction of the two liquids should show a faint yellow ring of $Ag_3AsO_3$.

### Arsenic Arsenic, As$^V$ (salt for study, sodium arsenate, $Na_3AsO_4$).

1. $H_2S$ precipitates, from strong HCl solutions (2 parts concentrated HCl to 1 part water), yellow arsenic sulphide, $As_2S_5$. $H_2S$ will precipitate $As_2S_5$ from dilute solutions of HCl if they are warmed to about 70° and the gas is passed through for some time. $As_2S_5$ behaves much like $As_2S_3$ towards $(NH_4)_2S_x$, aqua regia, and $(NH_4)_2CO_3$.

$As_2S_5$ is a colloidal precipitate and requires for its precipitation both heat and strong acid solution. (See Washing, p. 29.) The semi-solid often colors the solution yellow without precipitation; in which event it is necessary to add more HCl and increase the heat. Furthermore, $H_2S$ with cold dilute HCl does

not precipitate $As_2S_5$ very well, as the arsenic is reduced to the *-ous* condition: $Na_3AsO_4 + H_2S = Na_3AsO_3 + H_2O + S$.

2. **AgNO$_3$** precipitates from a very slightly alkaline solution, brown silver arsenate, $Ag_3AsO_4$, soluble in excess of $NH_4OH$ and $HNO_3$.

3. **MgSO$_4$** in presence of $NH_4Cl$ and $NH_4OH$ precipitates ammonium magnesium arsenate, $NH_4MgAsO_4$.[1]

The purpose of adding $NH_4Cl$ is to avoid the formation of the insoluble compound $Mg(OH)_2$; and the purpose of adding an excess of $NH_4OH$ is to insure the insolubility of the double salt $NH_4MgAsO_4$.

4. **(NH$_4$)$_2$MoO$_4$** in $HNO_3$ solution precipitates yellow ammonium arseno-molybdate, $(MoO_3)_{12}(NH_4)_3AsO_4$. The precipitation does not occur in the cold, like that from phosphoric acid (which see).

$(NH_4)_2MoO_4$ in $HNO_3$ solution changes to the more complex salt $(NH_4)_2Mo_4O_{13}$, which, with $H_3AsO_4$, forms insoluble $(MoO_3)_{12} \cdot (NH_4)_3AsO_4$. The reagent should be added in large excess (about $4 : 1$), as the precipitate is soluble in $H_3AsO_4$.

5. Similar to 4, under arsenious compounds.

6. Similar to 5, under arsenious compounds.

### Antimony (salt for study, antimonious chloride, SbCl$_3$).

1. **H$_2$S** precipitates orange antimonious sulphide, $Sb_2S_3$, soluble in $(NH_4)_2S_x$, hot concentrated HCl, and aqua regia; insoluble in $(NH_4)_2CO_3$.

2. **NH$_4$OH** and **NaOH** precipitate white antimonious hydroxide, $Sb(OH)_3$, soluble in excess of NaOH.

3. **AgNO$_3$** precipitates from alkaline solutions of antimonious salts a black mixture of $Ag_2O$ and metallic

silver. From antimonic salts, $AgNO_3$ precipitates white silver antimonate, $Ag_3SbO_4$, soluble in $NH_4OH$. These reactions are useful for detecting the -*ous* and the -*ic* conditions of antimony.

4. **Heating** on charcoal with fusion mixture gives a metallic antimony bead with white incrustation of $Sb_2O_3$.

5. **Water** in large excess hydrolyzes soluble antimonious salts and forms white insoluble basic salts : —

$$SbCl_3 + H_2O = SbOCl + 2\,HCl.$$
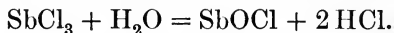
6. **Nascent hydrogen** reduces antimony compounds to stibine, $SbH_3$, and deposits metallic antimony on kindling, like arsenic. If $SbH_3$ is passed into a solution of $AgNO_3$, black silver antimonide, $SbAg_3$, will be precipitated : —

$$3\,AgNO_3 + SbH_3 = SbAg_3 + 3\,HNO_3.$$
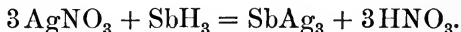
On account of the likeness between the reactions of arsenic and antimony with nascent hydrogen, it is well to compare the behaviors of the two metals in Marsh's test.

(*a*) The hydrogen flame is not tinted violet by $SbH_3$.

(*b*) The black antimony spots on cold porcelain are blacker and less lustrous than those of arsenic. Antimony spots are not removed by hypochlorite solutions.

(*c*) $H_2S$ passed through the hard glass tube containing antimony stain produces orange $Sb_2S_3$.

(*d*) In Hofmann's test, $SbH_3$ passed into $AgNO_3$ solution precipitates black $SbAg_3$. When the precipitation is completed, decant the liquid and wash the residue by

decantation.   Dissolve the antimony by boiling with a strong solution of tartaric acid to which a few drops of $HNO_3$ have been added.   Filter, acidify with HCl, and pass $H_2S$ through the warmed solution. . An orange precipitate indicates $Sb_2S_3$.

### Stannous Tin, Sn″ (salt for study, stannous chloride, $SnCl_2$).

1. **$H_2S$** precipitates brown stannous sulphide, SnS, soluble in $(NH_4)_2S_x$ and hot concentrated HCl; insoluble in dilute cold HCl and $(NH_4)_2CO_3$.

2. **$NH_4OH$** and **NaOH** precipitate white stannous hydroxide, $Sn(OH)_2$, soluble in excess of NaOH, forming sodium stannite, $Na_2SnO_2$.

3. **$HgCl_2$** freely added precipitates white $Hg_2Cl_2$.

4. **Metallic zinc** deposits metallic tin.

5. **Heating** on charcoal with fusion mixture gives metallic tin and a white incrustation of $SnO_2$.

### Stannic Tin, Sn″ᴵⱽ (salt for analysis, stannic chloride, $SnCl_4$).

1. **$H_2S$** precipitates yellow stannic sulphide, $SnS_2$, soluble in $(NH_4)_2S_x$ and hot concentrated HCl; insoluble in dilute cold HCl and $(NH_4)_2CO_3$.

2. **$NH_4OH$** and **NaOH** precipitate white stannic hydroxide, $SnO(OH)_2$, soluble in excess NaOH.

3. Similar to 4, under stannous salts.

4. Similar to 5, under stannous salts.

### PROCESS OF SEPARATION

The group is divided into two sub-groups. Sub-group $A$: arsenic, antimony, and tin, — metals whose sulphides are soluble in $(NH_4)_2S_x$. Sub-group $B$: mercury, lead, bismuth, copper, and cadmium, — metals whose sulphides are not soluble in $(NH_4)_2S_x$.

The separation of the members of Sub-group $A$ depends upon the following properties : —

(*a*) Insolubility of arsenic sulphide in boiling HCl, or the solubility of arsenic sulphide in $(NH_4)_2CO_3$ solution.

(*b*) Insolubility of metallic antimony in dilute HCl.

(*c*) Hofmann's separation of arsenic, antimony, and tin.

The separation of Sub-group $B$ depends upon the following properties : —

(*a*) Insolubility of HgS in boiling dilute $HNO_3$ ;

(*b*)    "    " $PbSO_4$ in acidified solution ;

(*c*)    "    " $(BiO)OH$ in $NH_4OH$ solution ;

(*d*)    "    " CuS in dilute $H_2SO_4$, or

     "    " CdS in KCN solution.

Into the solution[1] acidified with HCl[2] and warmed to about 70°, pass a constant stream of $H_2S$ for about fifteen minutes ; then cool the diluted solution, and before filtering pass $H_2S$ again till the precipitation is completed. The precipitation of $As_2S_3$ and $As_2S_5$ requires heat and a strongly acid (HCl) solution, both of which tend to dissolve the other sulphides. Hence it is necessary to cool and dilute the solution in order to precipitate all the sulphides.[3] Filter. The filtrate (*a*)[4]

may contain members of subsequent groups. The residue (*a*) may consist of the sulphides of all the members of the group. Thoroughly wash the residue with the aid of the suction pump, remove it from the paper and digest it with $(NH_4)_2S_x$[1] (or with $Na_2S_x$,[2] if the presence of copper is suspected) for about ten minutes. Filter and wash the residue with water containing some $(NH_4)_2S_x$, rejecting the washings. The filtrate (*b*) may contain the sulpho-salts of Sub-group *A*. The residue (*b*) may consist of the sulphides of Sub-group *B*.

**Separation of Sub-group A.** — To the filtrate (*b*) add dilute HCl till acid. Filter and reject the filtrate and washings. A yellow precipitate, residue (*c*), indicates the presence of members of the sub-group, or it may be sulphur or a mixture of the sulphides and sulphur. Sulphur can be dissolved by shaking the precipitate with benzol or petroleum ether. If all the precipitate dissolves, it is only separated sulphur. Two methods can be used for the further separation of Sub-group *A*.

*Method 1.* — Treat residue (*c*), possibly consisting of the reprecipitated sulphides, with warm concentrated HCl (concentrated HCl and a little water). Filter. The filtrate (*a'*) may contain antimony and tin chlorides. The residue (*a'*) may be sulphur and $As_2S_5$. Divide the residue into two parts. First part: Dry the yellow mass and heat in a closed tube with $Na_2CO_3$ and KCN. A mirror on the sides of the tube indicates arsenic. Second part: Fuse with $Na_2CO_3$ on a platinum foil; dissolve in $HNO_3$ and boil to expel carbonic acid. Add excess of $(NH_4)_2MoO_4$[3] solution in $HNO_3$ and boil. A yellow precipitate confirms the presence of arsenic.

Boil filtrate ($a'$) to expel $H_2S$. Transfer to a small dish, and immerse in the solution a galvanic couple of strips of zinc[1] and platinum. After the evolution of gas, black antimony coats the platinum and gray tin loosely adheres to the zinc. Wash the platinum and boil with tartaric acid and a drop of fuming $HNO_3$. $H_2S$ producing an orange precipitate confirms antimony. With the fingers rub off the loose tin from the zinc[2] into a dish. Again introduce the platinum and some HCl, and boil till all the loose tin dissolves. (Some insoluble particles of carbon may remain.) Filter, if necessary, and pour into a test-tube rinsed with $HgCl_2$. A white precipitate turning gray on boiling confirms tin.

### CHEMISTRY OF SULPHO-COMPOUNDS

The solution of the sulphides of arsenic, antimony, and tin by $(NH_4)_2S_x$ is due to the formation of the sulpho-salts of these elements. They occur in the periodic system about midway between the acid-producing and base-producing elements. Hence their oxides are generally basic with reference to strong acid oxides, and acid with reference to strong basic oxides. In the presence of strong bases, the oxides $As_2O_3$, $As_2O_5$, $Sb_2O_3$, $Sb_2O_5$, SnO, and $SnO_2$ form classes of *-ous* and *-ic* salts: —

$As_2O_3 + 6\,NaOH = 3\,H_2O + 2\,Na_3AsO_3$, sodium arsenite;
$As_2O_3 + 2\,NaOH = H_2O + 2\,NaAsO_2$,    "    metarsenite;
$As_2O_5 + 6\,NaOH = 3\,H_2O + 2\,Na_3AsO_4$,    "    arsenate;
$Sb_2O_3 + 6\,NaOH = 3\,H_2O + 2\,Na_3SbO_3$,    "    antimonite;
$Sb_2O_3 + 2\,NaOH = H_2O + 2\,NaSbO_2$,    "    metantimonite;
$Sb_2O_5 + 6\,NaOH = 3\,H_2O + 2\,Na_3SbO_4$,    "    antimonate;
$2\,SnO + 2\,NaOH = H_2O + Na_2Sn_2O_3(?)$, "    oxystannite;
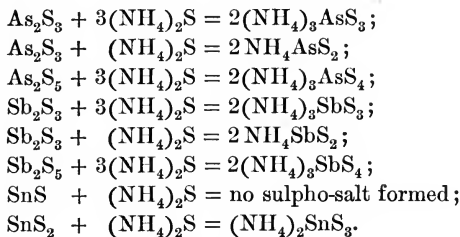$SnO_2 + 2\,NaOH = H_2O + Na_2SnO_3$,    "    stannate.
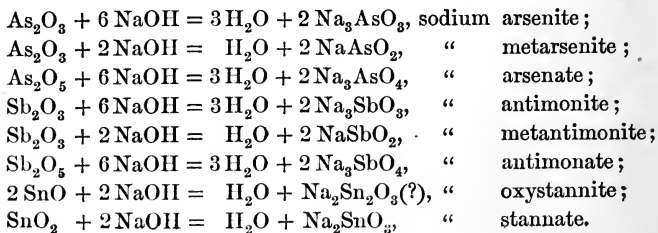
The corresponding soluble sulpho- or thio-salts are made in two ways:—

First: Reactions of $H_2S$ with the oxy-salts of the elements:—

$Na_3AsO_3 + 3H_2S = 3H_2O + Na_3AsS_3$, sodium sulpharsenite;
$NaAsO_2 + 2H_2S = 2H_2O + NaAsS_2$, " metasulpharsenite;
$Na_3AsO_4 + 4H_2S = 4H_2O + Na_3AsS_4$, " sulpharsenate; etc.
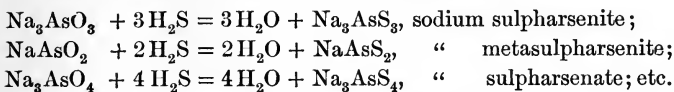
When the sulpho-salts are treated with HCl the hypothetical sulpho-acids are formed, but are immediately broken down to the insoluble sulphides. This is one reason that the presence of HCl is necessary for the precipitation of the sulphides by $H_2S$.

Second: Reactions of alkali sulphides with the sulphides of the elements:—

$$As_2S_3 + 3(NH_4)_2S = 2(NH_4)_3AsS_3;$$
$$As_2S_3 + (NH_4)_2S = 2NH_4AsS_2;$$
$$As_2S_5 + 3(NH_4)_2S = 2(NH_4)_3AsS_4;$$
$$Sb_2S_3 + 3(NH_4)_2S = 2(NH_4)_3SbS_3;$$
$$Sb_2S_3 + (NH_4)_2S = 2NH_4SbS_2;$$
$$Sb_2S_5 + 3(NH_4)_2S = 2(NH_4)_3SbS_4;$$
$$SnS + (NH_4)_2S = \text{no sulpho-salt formed};$$
$$SnS_2 + (NH_4)_2S = (NH_4)_2SnS_3.$$

All of the higher sulphides readily unite with $(NH_4)_2S$ to form -*ate* salts, but the lower sulphides unite with $(NH_4)_2S$ with varying difficulty.

$As_2S_3$ reacts with $(NH_4)_2S$ very readily;
$Sb_2S_3$ " " " with difficulty;
$SnS$ " " " not at all.
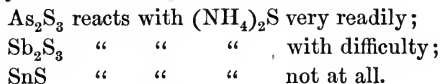
Hence, in order to change all the insoluble sulphides to soluble sulpho-salts, it is necessary to add ammonium polysulphide, $(NH_4)_2S_x$, so as to supply sufficient sulphur to convert all of the sulphides to the -*ate* salts:—

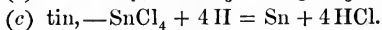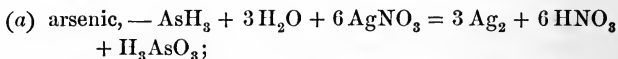$$As_2S_3 + 3(NH_4)_2S_x = 2(NH_4)_3AsS_4 + (3X-5)S;$$
$$As_2S_5 + 3(NH_4)_2S_x = 2(NH_4)_3AsS_4 + 3(X-1)S;$$
$$Sb_2S_3 + 3(NH_4)_2S_x = 2(NH_4)_3SbS_4 + (3X-5)S;$$
$$SnS + (NH_4)_2S_x = (NH_4)_2SnS_3 + (X-2)S;$$
$$SnS_2 + (NH_4)_2S_x = (NH_4)_2SnS_3 + (X-1)S.$$
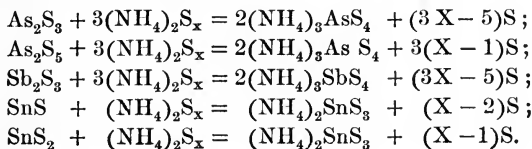
As stated above, these soluble sulpho-salts are readily decomposed by HCl and the sulphides reclaimed : —

$$2(NH_4)_3AsS_4 + 6 HCl = As_2S_5 + 6 NH_4Cl + 3 H_2S ;$$
$$2(NH_4)_3SbS_4 + 6 HCl = Sb_2S_5 + 6 NH_4Cl + 3 H_2S, \text{ etc.}$$
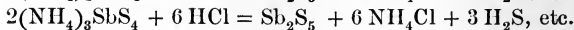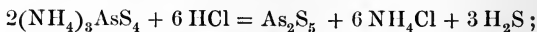
*Method 2, Hofmann's Separation.* — Dissolve the mixed sulphides with HCl and a crystal of $KClO_3$, and evaporate the chlorine and excess of acids. Arrange the apparatus for Hofmann's modification of Marsh's Test and add the dissolved sulphides to the contents of the generating flask. When the evolution of the gas has ceased, filter the contents of the test-tube. The black residue may consist of metallic silver and $SbAg_3$. Test for $SbAg_3$ by dissolving in tartaric acid, etc. The filtrate may contain the hypothetical acid $H_3AsO_3$ with excess of $AgNO_3$, which can be tested by producing yellow $Ag_3AsO_3$ with dilute $NH_4OH$. Filter the contents of the generating flask, remove the undissolved zinc, and test the residue for tin by dissolving in a small amount of HCl and then adding $HgCl_2$.

The reactions involved in the separation of arsenic, antimony, and tin by Hofmann's method are for : —

(a) arsenic, — $AsH_3 + 3 H_2O + 6 AgNO_3 = 3 Ag_2 + 6 HNO_3 + H_3AsO_3$;
(b) antimony, — $SbH_3 + 3 AgNO_3 = SbAg_3 + 3 HNO_3$;
(c) tin, — $SnCl_4 + 4 H = Sn + 4 HCl$.

**Separation of Sub-group B.** — Transfer the residue (b), supposed to consist of the members of the sub-group, to an evaporating dish, and boil with $HNO_3$[1] (diluted 1:2) till the chemical action ceases. Filter. The

residue $(a')$[1] may be black HgS or a mixture of HgS and white $Hg(NO_3)_2 \cdot 2\,HgS$. Dissolve in aqua regia, boil off the chlorine and excess of acids, and test with $SnCl_2$. The filtrate $(a')$ may contain $Pb(NO_3)_2$, $Bi(NO_3)_3$, $Cu(NO_3)_2$, and $Cd(NO_3)_2$. Concentrate this filtrate until most of the $HNO_3$ is driven off, add dilute $H_2SO_4$,[2] warm gently, and allow to stand for some time. A white precipitate is $PbSO_4$.[3] If lead is present, add an excess of dilute $H_2SO_4$ and evaporate till all the $HNO_3$ is expelled. Dilute with water, place aside to enable the precipitate to settle, and filter off the insoluble residue $(b')$. Test it by boiling with $NH_4C_2H_3O_2$ and adding $K_2CrO_4$. A yellow precipitate confirms $PbCrO_4$. If lead is present, use the filtrate from $PbSO_4$; if lead is absent, boil off excess of $HNO_3$ from filtrate $(a')$. Add $NH_4OH$ till alkaline. A blue fluid confirms the presence of copper and a white flocculent precipitate, bismuth. Filter.[4] Dissolve the residue $(c')$ in a few drops of HCl and test for BiOCl[5] by adding an excess of water. If the filtrate $(c')$ is blue, add a dilute solution of KCN carefully till the color disappears. Often copper is present in small quantities, and the blue[6] color is not distinct. In this event evaporate a small quantity of the filtrate almost to dryness, acidify with very dilute HCl, and add $K_4Fe(CN)_6$. A brown precipitate or coloration indicates $Cu_2Fe(CN)_6$. If copper is present, add very little dilute KCN solution. If copper is absent, adding KCN is not necessary. Pass $H_2S$. A yellow[7] precipitate confirms CdS.

# CHAPTER IX

## METALS OF GROUP III: ALUMINUM, CHROMIUM, AND IRON

CHARACTERISTIC: **Insolubility of the hydroxides in alkaline ($NH_4OH$) solution in the presence of ammonium chloride.**

GROUP REAGENT: **Ammonium hydroxide with ammonium chloride.**

### REACTIONS

## Aluminum (salt for study, aluminum sulphate, $Al_2(SO_4)_3$).

1. **$NH_4OH$** precipitates gelatinous aluminum hydroxide, $Al(OH)_3$, soluble somewhat in excess of reagent in the cold, but wholly insoluble if $NH_4Cl$ is present or if the solution is boiled.

2. **NaOH** acts like **$NH_4OH$**, except that $Al(OH)_3$ is completely dissolved in excess of reagent, forming sodium aluminate, $Na_3AlO_3$. This in turn is reconverted into insoluble $Al(OH)_3$ if the solution is boiled with $NH_4Cl$.

3. **$BaCO_3$**, suspended in water, precipitates aluminum completely in the cold as $Al(OH)_3$ mixed with a basic salt, probably $Al(OH)CO_3$.

4. **$(NH_4)_2S$** precipitates $Al(OH)_3$ with evolution of $H_2S$.

5. **$HNa_2PO_4$** precipitates white aluminum phosphate, $AlPO_4 \cdot H_2O$, soluble in alkalies in the absence of $NH_4Cl$ and in HCl and $HNO_3$; insoluble in $HC_2H_3O_2$.

6. **Spectrum** (see Special Method for Aluminum, p. 62).
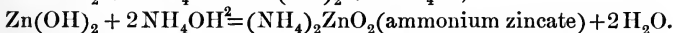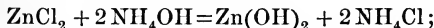
### INFLUENCE OF AMMONIUM SALTS[1]

The reactions between many salts and alkalies in the presence of ammonium compounds demand the following further explanation.

Soluble alkalies react with salts of many metals to produce hydroxides of various solubilities. Some of the more insoluble of these behave as weak acids in the presence of strong bases and combine with them to form new classes of soluble salts.

The following is a type of this class of reactions : —

$$ZnCl_2 + 2\,NaOH = Zn(OH)_2 + 2\,NaCl;$$
$$Zn(OH)_2 + 2\,NaOH = Na_2ZnO_2 \text{ (sodium zincate)} + 2\,H_2O.$$
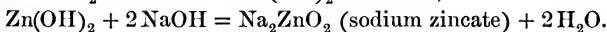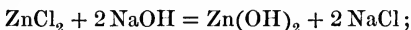
Ammonia behaves much like the other soluble bases, provided certain precautions are observed. The following reactions can occur : —

$$ZnCl_2 + 2\,NH_4OH = Zn(OH)_2 + 2\,NH_4Cl;$$
$$Zn(OH)_2 + 2\,NH_4OH = (NH_4)_2ZnO_2 \text{(ammonium zincate)} + 2\,H_2O.$$

The last reaction is interrupted in two ways : —

First : $NH_3$ splits off easily, thus allowing $Zn(OH)_2$ to be reclaimed. Second : the by-product, $NH_4Cl$, strongly influences the reaction and redissolves the precipitated $Zn(HO)_2$.

In order to obtain $(NH_4)_2ZnO_2$ it is necessary to add $NH_4OH$ to a *cold* solution of $ZnCl_2$, to avoid decomposition of $(NH_4)_2ZnO_2$ into $NH_3$ and $Zn(OH)_2$, and to filter off the solution of $NH_4Cl$. When an excess of $NH_4Cl$ or other ammonium salt is added, all of these conditions of solubility are modified. This applies to the reactions with the hydroxides of the alkali metals as well as ammonia.

In the case of the hydroxides of the bivalent metals, $Fe(OH)_2$, $Zn(OH)_2$, $Mn(OH)_2$, $Co(OH)_2$, $Ni(OH)_2$, $Ba(OH)_2$, $Sr(OH)_2$, $Ca(OH)_2$, and $Mg(OH)_2$, the tendency of the alkalies to redissolve them is greatly augmented by $NH_4Cl$. Hence these hydroxides are not precipitated in the presence of ammonium salts.
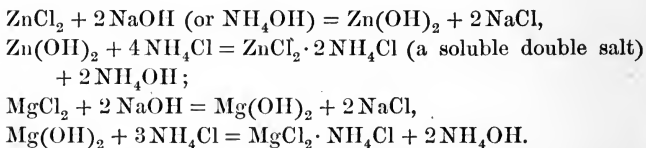
In the case of the hydroxides of the trivalent metals, $Al(OH)_3$, $Cr(OH)_3$, and $Fe(OH)_3$, the tendency of the alkalies to redissolve them is counteracted by $NH_4Cl$.

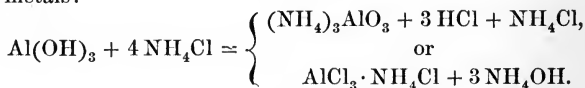Hence these hydroxides are completely precipitated in the presence of ammonium salts.

Two theories are now sanctioned by good authorities for the interpretation of the influence of ammonium salts in the reactions just mentioned.

### 1. Double Salts Theory

(a) **Salts of Bivalent Metals.** — The following pairs of reactions will explain this theory with reference to the salts of bivalent metals : —

$ZnCl_2 + 2NaOH$ (or $NH_4OH$) $= Zn(OH)_2 + 2NaCl,$
$Zn(OH)_2 + 4NH_4Cl = ZnCl_2 \cdot 2NH_4Cl$ (a soluble double salt)
$\quad + 2NH_4OH;$
$MgCl_2 + 2NaOH = Mg(OH)_2 + 2NaCl,$
$Mg(OH)_2 + 3NH_4Cl = MgCl_2 \cdot NH_4Cl + 2NH_4OH.$

(b) **Salts of Trivalent Metals.** — The application of equations analogous to those of the preceding paragraph would lead us to expect the following reactions to occur with hydroxides of trivalent metals : —

$$Al(OH)_3 + 4NH_4Cl \simeq \begin{cases} (NH_4)_3AlO_3 + 3HCl + NH_4Cl, \\ \qquad\qquad \text{or} \\ \quad AlCl_3 \cdot NH_4Cl + 3NH_4OH. \end{cases}$$

But the hypothetical, soluble bodies, $(NH_4)_3AlO_3$ and $AlCl_3 \cdot NH_4Cl$, are not known to exist, and their non-existence is taken to explain the failure of the hydroxides of trivalent metals to dissolve in the solutions of ammonium salts.

### 2. Ionic Theory

Another explanation of the part played by ammonium salts is based upon the simple ionic principle that the addition of an ion in common with one in the solute decreases the dissociation of the latter.

(a) **Salts of Bivalent Metals.** — When NaOH or $NH_4OH$ is added in excess to the solution of a bivalent metal, a precipitate

is formed which readily dissolves on the addition of $NH_4Cl$. The explanation is that the addition of the common ion, $NH_4$, suppresses the negative ion, OH, thus driving the dissociated ions into undissociated and inactive molecules of $NH_4OH$. As the hydroxides of the bivalent metals in question are usually moderately well dissociated, $NH_4Cl$ would not only suppress the free OH ions of any excess of $NH_4OH$, but also those of the hydroxides themselves. Of course it must be understood that if NaOH is used, this reaction first occurs : —

$$NaOH + NH_4Cl = NaCl + NH_4OH.$$
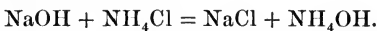
For application of the principle the important case of magnesium salts with $NH_4OH$ and $NH_4Cl$ is considered : —

Substituting in the equation $a \cdot b = c \cdot k$,[1] the equation

$$NH_4 \times OH = NH_4OH \times k, \text{ or } \frac{NH_4 \times OH}{NH_4OH} = k, \text{ is obtained.}$$

$NH_4$, OH, $NH_4OH$, and $k$ are, respectively, the positive and negative ions, the undissociated molecules, and the ionization constant for $NH_4OH$. Now when $NH_4Cl$ is introduced the number of $NH_4$ ions is greatly increased, and the result is to suppress the OH ions. By letting $x =$ number of $NH_4$ ions added, and $y =$ those of the undissociated molecules of $NH_4OH$ (resulting from the addition of $NH_4Cl$), the equation becomes : —

$$\frac{(NH_4 + x - y)\,(OH - y)}{NH_4OH + y} = k.$$

This decreases the number of OH ions and leaves only $(OH - y)$ for unit volume. It is owing to this disappearance of OH ions that $Mg(OH)_2$ is not precipitated, — too little molecular $Mg(OH)_2$ being formed to oversaturate the solution.

(b) **Salts of Trivalent Metals.** — When NaOH, $NH_4Cl$, and $AlCl_3$ are brought together the following reactions probably occur : —

$$AlCl_3 + 3\,NaOH = Al(OH)_3 + 3\,NaCl\,;$$
$$NaOH + NH_4Cl = NaCl + NH_4OH.$$
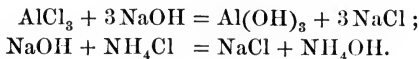
Now $Al(OH)_3$, unlike $Mg(OH)_2$ and hydroxides of some bivalent metals, is a very weak base and, consequently, very poorly dissociated. Hence, when an excess of $NH_4Cl$ is added, it suppresses only the OH ions of $NH_4OH$ — not those of $Al(OH)_3$. Thus $NH_4Cl$ not only does not affect the precipitated hydroxide but also destroys the power of $NH_4OH$ to dissolve it.

## Chromium (salt for study, chromium sulphate, $Cr_2(SO_4)_3$).

1. **$NH_4OH$**[1] gives reactions similar to 1, under aluminum.

2. **NaOH** gives reactions similar to 2, under aluminum.

3. **$BaCO_3$** gives reactions similar to 3, under aluminum, except that the precipitation requires more time for its completion.

4. **$(NH_4)_2S$** gives reactions similar to 4, under aluminum.

5. **Fusion** with fusion mixture on a platinum foil, or with sodium dioxide, $Na_2O_2$, on thick silver foil, gives a soluble yellow mass, containing sodium chromate, $Na_2CrO_4$.

6. **$Na_2O_2$** heated with a solution of a chromium salt gives yellow $Na_2CrO_4$.

7. **Borax bead** with both oxidizing and reducing flames gives a yellow-green coloration of sodium chromium metaborate, $Na_6Cr_2(BO_2)_{12}$.

Reactions 5 and 6 illustrate the conversion of chromium as a base-producing element to chromium as an acid-producing element.

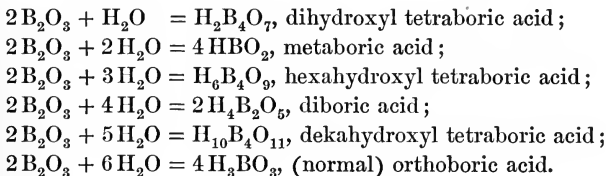There are two classes of chromium compounds derived from the two oxides $Cr_2O_3$ and $CrO_3$.

Chromic oxide, $Cr_2O_3$, is basic and forms salts with acids: $Cr_2O_3 + 6HCl = 2CrCl_3 + 3H_2O$. By oxidation $Cr_2O_3$ is changed to chromium trioxide, $CrO_3$, which is an anhydride and forms

salts with bases: $CrO_3 + 2 NaOH = Na_2CrO_4 + H_2O$. The oxidation of $Cr_2O_3$ in solution may be accomplished by $Na_2O_2$ or by hydrogen dioxide, $H_2O_2$. $CrO_3$ is a strong oxidizing agent and is easily reduced to $Cr_2O_3$ by various reagents, namely, $H_2S$, $SO_2$, HCl, and many organic compounds. If $H_2S$ is passed through an acidified (HCl) solution of potassium dichromate, $K_2Cr_2O_7$, there will be a change of color from red to green:
$K_2Cr_2O_7 + 3 H_2S + 8 HCl = 2 CrCl_3 + 2 KCl + 3 S + 7 H_2O$.

In this case chromium is changed from the acid to the basic condition.

## CHEMISTRY OF BORAX BEADS

Borax (sodium tetraborate, $Na_2B_4O_7 \cdot 10 H_2O$), like $Na_2CO_3$, is both an inactive flux, as in normal sodium borate, $Na_3BO_3$, and an active chemical agent, as in boric acid, $H_3BO_3$. (See Fusion, p. 43.) When borax is heated, it loses its water of crystallization and fuses to a clear bead on the platinum wire. If a metallic oxide or salt is fused with the clear bead, a double borate is formed, which is often colored. The reaction can be easily understood by a review of the principal hydroxyl acids of boron. Water unites with boric oxide, $B_2O_3$, increasing in an arithmetical progression to form a systematic chain of polyboric acids, of which the following are important in this connection: —

$2 B_2O_3 + H_2O\ \ = H_2B_4O_7$, dihydroxyl tetraboric acid;
$2 B_2O_3 + 2 H_2O = 4 HBO_2$, metaboric acid;
$2 B_2O_3 + 3 H_2O = H_6B_4O_9$, hexahydroxyl tetraboric acid;
$2 B_2O_3 + 4 H_2O = 2 H_4B_2O_5$, diboric acid;
$2 B_2O_3 + 5 H_2O = H_{10}B_4O_{11}$, dekahydroxyl tetraboric acid;
$2 B_2O_3 + 6 H_2O = 4 H_3BO_3$, (normal) orthoboric acid.

From these equations it can be seen that any succeeding acid in the list can be formed from the next preceding by the addition of one molecule of water; and the reverse is also true, that any higher acid can be formed from the next lower.

The corresponding salts of these acids are formed in a similar manner, provided the factor to be added is a metallic

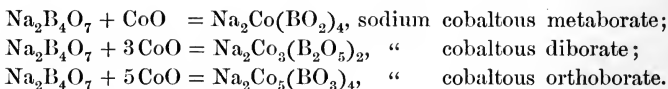oxide instead of water. The most important salts are given for illustration : —

$Na_2B_4O_7,$ sodium tetraborate (borax);

$Na_2B_4O_7 + Na_2O = 4\,NaBO_2,$ " metaborate;

$Na_2B_4O_7 + 3\,Na_2O = 2\,Na_4B_2O_5,$ " diborate;

$Na_2B_4O_7 + 5\,Na_2O = 4\,Na_3BO_3,$ " orthoborate.
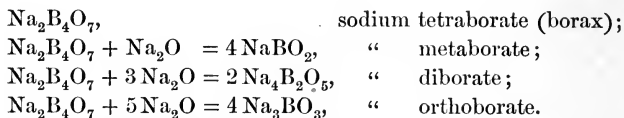
This further explains the statement above, that borax is both an inactive flux, like $Na_3BO_3$, and an active chemical agent, like $H_3BO_3$.

It is equivalent to four molecules of boric acid with one molecule of water replaced by sodium oxide, and the other five molecules of water displaced : —

$$4\,H_3BO_3 + Na_2O = Na_2B_4O_7 + 6\,H_2O.$$
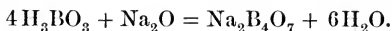
Thus it is in part a salt and in part an anhydride.

If an oxide of a heavy metal is substituted for $Na_2O$, double borates are formed : —

$Na_2B_4O_7 + CoO = Na_2Co(BO_2)_4,$ sodium cobaltous metaborate;

$Na_2B_4O_7 + 3\,CoO = Na_2Co_3(B_2O_5)_2,$ " cobaltous diborate;

$Na_2B_4O_7 + 5\,CoO = Na_2Co_5(BO_3)_4,$ " cobaltous orthoborate.

Or, in the case of the triad element chromium : —

$3\,Na_2B_4O_7 + Cr_2O_3 = Na_6Cr_2(BO_2)_{12},$ sodium chromic metaborate, etc.
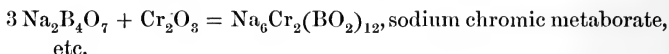
The metaborate, then, is the first product formed by adding a small quantity of the oxide to an excess of borax, while the orthoborate is the last formed by adding a larger amount of the oxide. What the actual composition of a given bead, made without weighing its components, may be can only be determined by a quantitative analysis. Probably every bead contains more or less of each of a large number of double borates. However, as the colors can be seen best by using small quantities of the oxides with a large excess of borax, the metaborates predominate, and as such the beads are usually represented.

The same laws which apply to the formation of polyborates apply to the formation of polyphosphates and silicates. Hence the vast number of natural and artificial silicates can be traced to their corresponding acids.

## Ferrous Iron, Fe″ (salt for study, ammonium ferrous sulphate, $(NH_4)_2Fe''(SO_4)_2$).

1. **$NH_4OH$** and **NaOH** precipitate ferrous hydroxide, $Fe(OH)_2$, which oxidizes quickly to brown ferric hydroxide, $Fe(OH)_3$. $NH_4Cl$ partly prevents the precipitation by $NH_4OH$, and partly that by NaOH.

2. **$(NH_4)_2S$** precipitates black ferrous sulphide, FeS.

3. **$K_4Fe(CN)_6$** precipitates white potassium ferrous ferrocyanide, $K_2Fe''Fe(CN)_6$, which rapidly oxidizes to Prussian blue.

4. **$K_3Fe(CN)_6$** precipitates Turnbull's blue, ferrous ferricyanide, $Fe_3''(Fe(CN)_6)_2$.

5. **Borax bead** with the oxidizing flame gives a yellow coloration, $Na_6Fe_2'''(BO_2)_{12}$; with the reducing flame, a green coloration, $Na_2Fe''(BO_2)_4$.

## Ferric Iron, Fe‴ (salt for study, ferric chloride, $FeCl_3$).

1. **$NH_4OH$** and **NaOH** precipitate brown ferric hydroxide, $Fe(OH)_3$, insoluble in excess of reagents. $NH_4Cl$ does not prevent the precipitation either by $NH_4OH$ or by NaOH.

2. **$BaCO_3$** precipitates a brown basic salt, $Fe_2O(CO_3)_2$.

3. **$H_2S$** reduces ferric to ferrous salts and precipitates free sulphur: —

$$2\,FeCl_3 + H_2S = 2\,FeCl_2 + 2\,HCl + S.$$
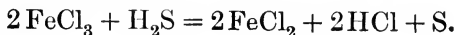
The precipitate of sulphur formed in this reaction is sometimes mistaken for the sulphides of certain members of Group II. This confusion will not occur if it is recalled that the members of Group II are all colored, whereas a precipitate of finely divided sulphur is white.

4. $(NH_4)_2S$ reduces ferric to ferrous salts and precipitates ferrous sulphide: —

$$2\,FeCl_3 + 3\,(NH_4)_2S = 2\,FeS + 6\,NH_4Cl + S.$$
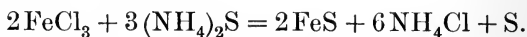
5. $K_4Fe(CN)_6$ precipitates Prussian blue, ferric ferrocyanide, $Fe_4'''(Fe(CN)_6)_3$.

6. $K_3Fe(CN)_6$ gives a brown coloration.

7. KCNS gives a deep-red coloration, ferric sulphocyanate, $Fe(CNS)_3$.[1]

8. Borax bead gives the same results as with ferrous salts.

### PROCESS OF SEPARATION

The separation of the members of this group is based upon the facts that $Cr(OH)_3$ is oxidized to soluble $Na_2CrO_4$ by means of $Na_2O_2$ or by fusion with the mixture of $Na_2CO_3$ and $KNO_3$, and that $Al(OH)_3$ is soluble in an excess of NaOH. Two methods of making the separation are given, of which the first and simpler is to be employed in the absence of phosphoric, boric, silicic, and hydrofluoric acids; whereas the second and more complicated method is to be followed in the presence of these bodies.[2]

Boil off all traces of $H_2S$, testing for its removal by holding above the liquid a strip of paper moistened with $AgNO_3$ or $Pb(NO_3)_2$. It must be driven off

completely; since, if it were allowed to remain, the members of Group IV would be precipitated out of due course upon the addition of $NH_4OH$, the precipitant for the members of Group III. Next test for iron by adding $K_3Fe(CN)_6$ to a small portion of the solution; and in case it is present add a few drops of $HNO_3$ and boil until the reaction for ferrous compounds disappears. The oxidation of iron to the ferric state at this point is necessary, since, if left in the ferrous state, it would not be precipitated by $NH_4OH$ in presence of $NH_4Cl$.

The solution should now be tested for oxalic acid or other organic matter by evaporating a small portion of the solution to dryness, and heating the residue in a closed tube connected with a small rubber delivery tube, through which any gas that may be evolved can be conducted into lime water. A charred residue in the closed tube and a white precipitate in the lime water indicate the presence of organic compounds.[1] If such are found, evaporate the whole solution to dryness and heat the residue with the addition of a few drops of sulphuric acid, until the organic matter is thoroughly decomposed. Cover the residue with

[1] In testing for organic matter blackening is not conclusive. Many inorganic salts, among them those of iron, nickel, cobalt, and manganese, blacken when heated. Furthermore, a failure to blacken is not an evidence of the absence of organic compounds, since some of them which contain a large per cent of oxygen — oxalates in particular — do not char, but give off all their carbon as oxides. The lime-water test, too, is not absolute, though more reliable than that by charring. Compounds evolving oxides of sulphur also whiten lime water. But both tests are good *signs;* and as gentle ignition is also the means of eliminating silicic acid, it is best to evaporate and ignite the solution even when the presence of organic acids is doubtful.

concentrated HCl, evaporated almost to dryness, add water and a few drops of concentrated $HNO_3$, and boil. Filter the solution from the separated carbon and silica.

Phosphoric acid[1] must next be tested for by warming a small portion of the filtrate with an excess of $HNO_3$ solution of $(NH_4)_2MoO_4$. Should it be present, barium must also be tested for at this stage by making a small portion alkaline with $NH_4OH$, acidifying with $HC_2H_3O_2$, and testing for barium with $K_2CrO_4$. Next add $NH_4Cl$,[2] boil, and add $NH_4OH$ till its odor persists. Filter quickly while hot. Reserve filtrate (*a*) for subsequent groups. Redissolve residue (*a*) in least quantity of HCl, nearly neutralize with $Na_2CO_3$, transfer to a stoppered flask, and add when cold a large excess of suspended $BaCO_3$.[3] Shake from time to time, and filter after 15 minutes. If phosphoric acid is present, combine filtrates (*a*) and (*b*)[4]; if absent, test filtrate (*b*) for manganese by evaporating to dryness and fusing with $Na_2CO_3$ and $KNO_3$. Residue (*b*) may consist of basic salts of Group III, if phosphoric acid is absent; or, if present, it may also contain phosphates of metals of Groups III, IV, V, and of magnesium.

### In Absence of Phosphates

*Method 1.* Thoroughly wash the residue (*b*) and transfer to a test-tube. Add a small quantity of water and some bits of $Na_2O_2$, and boil till effervescence ceases. Filter and wash. The residue (*c*) may be brown $Fe(OH)_3$, whose identity can be confirmed by dissolving in dilute HCl and testing with $K_4Fe(CN)_6$. The filtrate (*c*) may contain yellow $Na_2CrO_4$ and $Na_3AlO_3$.

The following equations explain the formation of the soluble salts : —

$$3\,Na_2O_2 + 2\,Cr(OH)_3 = 2\,Na_2CrO_4 + 2\,H_2O + 2\,NaOH\,;$$
$$6\,NaOH + 2\,Al(OH)_3 = 2\,Na_3AlO_3 + 6\,H_2O.$$
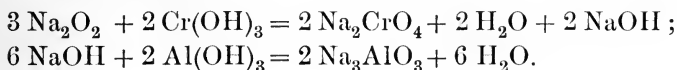
Divide the filtrate (*c*) into two parts. Acidify the one with $HC_2H_3O_2$ and test for chromium by adding $Pb(C_2H_3O_2)_2$. Acidify the other part with dilute HCl, and while boiling test for aluminum by adding an excess of $NH_4OH$, — or to the second part of the filtrate add some $NH_4Cl$ and boil. After cooling, a gelatinous precipitate confirms presence of aluminum.

*Method 2.* Dry residue (*b*) and fuse in a platinum crucible or foil with an excess of fusion mixture. The cooled mass is triturated in a mortar, — preferably a glass one, — is digested with water for fifteen minutes, and then is filtered. The residue (*c*) is tested for iron, and the filtrate (*c*) for chromium and aluminum, as in Method 1. In case of doubt test the solution for aluminum with the spectroscope.

## In Presence of Phosphates

Dissolve residue (*b*) in a little HCl, nearly neutralize by cautious addition of $Na_2CO_3$, add $NaC_2H_3O_2$ and $HC_2H_3O_2$, and boil and filter. The filtrate (*c*) may contain phosphates of the metals of Groups IV and V, and of magnesium. The residue (*c*) may consist of the phosphates of aluminum, chromium, and iron. To the filtrate (*c*) add dilute $FeCl_3$, drop by drop, until a red coloration appears. At this point, precipitation of

$FePO_4$ is completed.  The red color indicates the formation of $Fe(C_2H_3O_2)_3$, an excess of which would redissolve the $FePO_4$.  Hence the solution should now be boiled in order to change any excess of $Fe(C_2H_3O_2)_3$ to an insoluble basic acetate, $FeO(C_2H_3O_2)$.  It is necessary to filter the mixture with the pump while hot, as $FeO(C_2H_3O_2)$ redissolves to $Fe(C_2H_3O_2)_3$ on cooling. The filtrate (*d*) may contain the chlorides of Groups IV and V, and of magnesium.  This filtrate should be combined with filtrate (*a*) and afterwards tested for subsequent groups.  The residue (*c*), possibly consisting of $FePO_4$ and some $FeO(C_2H_3O_2)$, should be rejected.

The separation of the members of Group III, which may be present as phosphates in residue (*b*), can now be made without difficulty by either of the procedures, Methods 1 and 2.

The following further explanations may be given concerning the method of analysis in presence of phosphates : —

It will be seen, on reference to the Table of Solubilities given on p. 34, that the phosphates of Mg, Ba, Sr, Ca, Co, Ni, Mn, and Zn are all more or less insoluble in water or alkaline solutions. If present in an acid solution, they therefore will be thrown out upon neutralization ; and if this solution be under examination for the members of Group III, they will separate simultaneously with the hydroxides of this group.  Hence the necessity of following the modified method of analysis in their presence.  They play so important a part in the separation of the members of Group III that the student is advised to perform in advance the exercises with phosphoric acid, given on p. 135, in order that he may have some practical knowledge of their reactions.

In removing phosphoric acid after almost neutralizing the HCl solution with $Na_2CO_3$, $NaC_2H_3O_2$ is added to destroy the solvent effect of HCl, which dissolves all of the phosphates.  $HC_2H_3O_2$,

which is set free from $NaC_2H_3O_2$ by metathesis with HCl, dissolves only the phosphates of Groups IV and V, and magnesium, — not those of Group III. But, though $HC_2H_3O_2$ is set free, its acid effects are greatly weakened by the presence of an excess of a salt having an ion in common with it; and for this reason some free $HC_2H_3O_2$ must be added with $NaC_2H_3O_2$, though a large excess of the acid should be avoided, as $CrPO_4$ is sparingly soluble in it. (See Question 5, Theory of Solutions, p. 22.)

# CHAPTER X

## METALS OF GROUP IV: ZINC, MANGANESE, COBALT, AND NICKEL

CHARACTERISTIC: **Insolubility of the sulphides in alkaline solution.**

GROUP REAGENT: **Ammonium sulphide in presence of ammonium hydroxide and ammonium chloride.**

### REACTIONS

### Zinc (salt for study, zinc sulphate, $ZnSO_4$).

1. $(NH_4)_2S$ precipitates white zinc sulphide, $ZnS$, soluble in strong acids; insoluble in alkalies and $HC_2H_3O_2$. The precipitation is hastened in dilute solutions by presence of $NH_4Cl$.

2. **NH$_4$OH** and **NaOH** precipitate white zinc hydroxide, $Zn(OH)_2$, soluble in excess of reagent, forming ammonium zincate, $(NH_4)_2ZnO_2$,[1] or sodium zincate, $Na_2ZnO_2$. $NH_4Cl$ solutions dissolve $Zn(OH)_2$.

3. **Reducing flame** on charcoal with $Na_2CO_3$ gives a yellow incrustation of zinc oxide, $ZnO$, turning white on cooling. If this coating is moistened with cobalt nitrate and again heated with the blowpipe, a green coloration will appear, due to a double oxide of zinc and cobalt.

### Manganese (salt for study, manganese sulphate, $MnSO_4$).

1. $(NH_4)_2S$ precipitates pink[2] manganous sulphide, $MnS$, soluble in acids, including $HC_2H_3O_2$; insoluble in alkalies. $NH_4Cl$ assists precipitation.

2. **NH₄OH** and **NaOH** precipitate manganous hydroxide, $Mn(OH)_2$, which oxidizes to brown hydrated manganic oxide, $Mn_2O_2(OH)_2$. $NH_4Cl$ partly redissolves $Mn(OH)_2$ if precipitated by $NH_4OH$, but only partially if precipitated by NaOH.

3. **Fusion** with $Na_2CO_3$ and $KNO_3$ on a platinum foil gives a soluble green mass of sodium manganate, $Na_2MnO_4$, changing to red sodium permanganate, $Na_2Mn_2O_8$, on heating or acidifying. This reaction is also produced by adding $Na_2O_2$ to the solution and warming till effervescence ceases.

4. **Boiling** with $PbO_2$ and $H_2SO_4$ gives a deep-red coloration of permanganic acid, $H_2Mn_2O_8$.

5. **Borax bead** in the oxidizing flame gives an amethyst coloration, sodium manganic metaborate, $Na_6Mn_2(BO_2)_{12}$. This color is destroyed by the reducing flame, due to the formation of manganous metaborate.

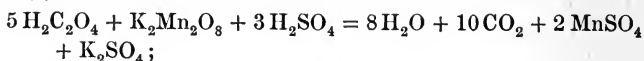6. **Spectrum** (see Special Method for Manganese, p. 63).

### CHEMISTRY OF MANGANESE COMPOUNDS

There are six important oxides of manganese having the following formulæ: $MnO$, $Mn_3O_4$, $Mn_2O_3$, $MnO_2$, $MnO_3$, $Mn_2O_7$. Of these, the first, second, and third are basic, the first forming manganous salts with acids, and the third, manganic salts. The fourth oxide is both basic and acid, forming manganous salts with loss of oxygen and also forming unstable manganites with more basic oxides. The fifth and sixth are acid oxides and produce, respectively, manganates and permanganates. The ready conversion of the lower basic oxides to the higher acid oxides by oxidation is of importance in qualitative analysis, on account of the solubility and characteristic colors of the salts of the higher oxides. Reactions 3, 4, and 5 illustrate these effects.
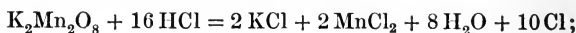
The higher oxides are also easily reduced to the lower, and for this reason are extensively used in quantitative analysis.

The following equations illustrate a few of the many cases of oxidation depending on the reduction of the higher oxides of manganese : —
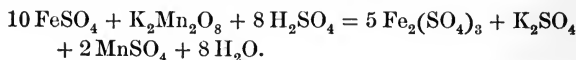
(*a*) Oxidation of oxalic acid : —

$$5\,H_2C_2O_4 + K_2Mn_2O_8 + 3\,H_2SO_4 = 8\,H_2O + 10\,CO_2 + 2\,MnSO_4 + K_2SO_4;$$

(*b*) Oxidation of hydrochloric acid : —

$$K_2Mn_2O_8 + 16\,HCl = 2\,KCl + 2\,MnCl_2 + 8\,H_2O + 10\,Cl;$$

(*c*) Oxidation of ferrous to ferric salts : —

$$10\,FeSO_4 + K_2Mn_2O_8 + 8\,H_2SO_4 = 5\,Fe_2(SO_4)_3 + K_2SO_4 + 2\,MnSO_4 + 8\,H_2O.$$

In all these cases the reduction of $K_2Mn_2O_8$ is accompanied by the destruction of the brilliant red color of the salt.

### Cobalt (salt for study, cobalt nitrate, $Co(NO_3)_2$).

1. **$(NH_4)_2S$** precipitates black cobaltous sulphide, CoS, insoluble in cold dilute HCl; soluble in $HNO_3$ and in aqua regia. The presence of $NH_4Cl$ aids the precipitation of CoS.

2. **$NH_4OH$** precipitates blue cobaltous hydroxide, $Co(OH)_2$, soluble to a brown fluid in excess of reagent. $NH_4Cl$ hinders the precipitation.

3. **NaOH** precipitates blue cobaltous hydroxide, $Co(OH)_2$, not soluble in excess of reagent. $NH_4Cl$ prevents precipitation.

4. **KCN** precipitates light-brown cobaltous cyanide, $Co(CN)_2$, soluble in excess of reagent with formation of potassium cobaltous cyanide, $K_4Co(CN)_6$. This compound is decomposed by acids, in the absence of

an excess of KCN, with reprecipitation of $Co(CN)_2$. If $K_4Co(CN)_6$ is oxidized with a mixture of NaOH and bromine water, containing NaBrO, it changes to the stable *-ic* salt, $K_3Co(CN)_6$, which will yield no precipitate with acids.

5. **KNO$_2$** added to the solution strongly acidified with $HC_2H_3O_2$ gives a yellow precipitate, potassium cobaltic nitrite, $K_3Co(NO_2)_6$. The precipitate will separate after some hours in a warm place.

$K_3Co(NO_2)_6$ is readily broken down by strong acids and alkalies, but is insoluble in $HC_2H_3O_2$ and in a solution of $KNO_2$. Hence, if strong acid is present, it is necessary to neutralize it with $Na_2CO_3$ and then to add an excess of $HC_2H_3O_2$ and $KNO_2$.

6. **Borax bead** with both the oxidizing and reducing flames gives a blue coloration of sodium cobaltous metaborate, $Na_2Co(BO_2)_4$.

### Nickel (salt for study, nickel chloride, NiCl$_2$).

1. **(NH$_4$)$_2$S** precipitates black nickel sulphide, NiS, sparingly soluble in excess of reagent; soluble in hot $HNO_3$ or aqua regia; almost insoluble in dilute HCl. The presence of $NH_4Cl$ aids the precipitation of NiS.

2. **NH$_4$OH** precipitates greenish nickelous hydroxide, $Ni(OH)_2$, soluble in excess of reagent, forming a blue fluid. $NH_4Cl$ prevents the precipitation.

3. **NaOH** precipitates $Ni(OH)_2$, insoluble in excess of reagent, but soluble in $NH_4Cl$.

4. **KCN** precipitates greenish nickelous cyanide, $Ni(CN)_2$, soluble in excess of reagent, forming potassium nickelous cyanide, $K_2Ni(CN)_4$. NaBrO does not

oxidize $K_2Ni(CN)_4$ to the corresponding *-ic* salt, but to black nickelic hydroxide, $Ni(OH)_3$.

5. **KNO₂** produces no precipitate with nickel salts.

6. **Borax bead** in the oxidizing flame gives yellow $Na_2Ni(BO_2)_4$; in the reducing flame it gives gray metallic nickel.

Why concentrated HCl does not dissolve CoS and NiS has not been satisfactorily explained. It would seem reasonable that as $H_2S$ does not precipitate the sulphides of cobalt and nickel from a solution of their chlorides, their sulphides should be soluble in HCl. It has been surmised that immediately after precipitation the sulphides undergo *polymerization*, *i.e.*, a locking together of several of their molecules, to form very insoluble compounds, $(CoS)_x$ and $(NiS)_x$.

## PROCESS OF SEPARATION

The separation of the members of this group is based upon the facts that $Zn(OH)_2$ is soluble in excess of NaOH; that MnS is soluble in $HC_2H_3O_2$; and that the borax bead, $KNO_2$, and KCN with NaBrO give distinctive reactions with cobalt and nickel salts. The process of separation is as follows: —

Boil off excess of $NH_4OH$, add $NH_4Cl$, and then $(NH_4)_2S$ in moderate excess. Filter and wash[1] thoroughly, rejecting the washings. The residue (*a*) may consist of the sulphides of the group. The filtrate (*a*) may contain members of Groups V and VI, and possibly Mn, which separates slowly from dilute solutions. MnS oxidizes readily to brown $Mn_2O_2(OH)_2$, — especially if in dilute solutions, or if the residue is exposed to the air for a short while, — and this may appear as

a brown precipitate [1] in the filtrate from the sulphides of Group IV. Therefore set this filtrate aside, and if such a precipitate appears, filter and preserve the filtrate to be tested for Groups V and VI.

Dissolve the residue (a) in boiling dilute HCl, to which a small crystal of $KClO_3$ is added. Continue the boiling till all free chlorine is expelled; then add while stirring an excess of NaOH. After cooling, filter. The filtrate (b) may contain $Na_2ZnO_2$, and the residue (b) may consist of $Mn(OH)_2$, $Co(OH)_2$, and $Ni(OH)_2$. Pass $H_2S$ through the filtrate (b). A white precipitate confirms the presence of zinc.

The washed residue (b) is dissolved in a small quantity of hot HCl. After nearly neutralizing with $NH_4OH$, some $NH_4C_2H_3O_2$ is added and $H_2S$ is passed till the precipitation is completed. Filter. The residue (c) may consist of CoS and NiS. The filtrate (c) may contain $Mn(C_2H_3O_2)_2$, and is to be concentrated to a small bulk and tested in either of the following ways : —

First: Add $NH_4OH$, $NH_4Cl$, and $(NH_4)_2S$. A yellow or green precipitate, appearing after some time, confirms MnS.

Second: Add a solution of $Na_2CO_3$, dissolve the white precipitate in HCl, and add $NH_4OH$, $NH_4Cl$, and $(NH_4)_2S$. In case of doubt, test the solution for manganese with the spectroscope.

Test the residue (c) with the borax bead for cobalt.

Dissolve the residue (c) in a very little aqua regia, evaporate off chlorine and excess of acids, and divide into two parts.

To one portion add $Na_2CO_3$ till alkaline, then $HC_2H_3O_2$ in excess, and finally add some solid $KNO_2$. After standing twenty-four hours in a warm place, a yellow precipitate confirms $K_3Co(NO_2)_6$. Filter and add excess of NaOH, which will precipitate $Ni(OH)_2$ if nickel is present.

Make the second part neutral by adding NaOH, testing with litmus paper ; then add KCN until the yellow precipitate redissolves. Digest with constant stirring for 10 minutes, or till the dark color disappears. Filter into a large test-tube, and add to the filtrate an equal bulk of NaOH and sufficient bromine water to produce a permanent red color. A black precipitate on gently warming confirms nickel.

# CHAPTER XI

## METALS OF GROUP V : BARIUM, STRONTIUM, AND CALCIUM

CHARACTERISTIC: **Insolubility of the carbonates in alkaline solution.**

GROUP REAGENT: **Ammonium carbonate in presence of ammonium hydroxide and ammonium chloride.**

### REACTIONS

### Barium (salt for study, barium nitrate, $Ba(NO_3)_2$).

1. $(NH_4)_2CO_3$ precipitates white barium carbonate, $BaCO_3$, soluble in acids (except $H_2SO_4$) and in acid ammonium carbonate, $H(NH_4)CO_3$. As $(NH_4)_2CO_3$ easily dissociates into $H(NH_4)CO_3$ and $NH_3$, it is necessary to add $NH_4OH$ before $(NH_4)_2CO_3$. $NH_4Cl$ solutions dissolve $BaCO_3$ slightly, — especially while boiling, — giving off $NH_3$ and $CO_2$.

2. $H_2SO_4$ (also $CaSO_4$ and $SrSO_4$) precipitates white barium sulphate, $BaSO_4$, insoluble in dilute acids and alkalies; somewhat soluble in hot concentrated acids.

3. $(NH_4)_2C_2O_4$ precipitates white barium oxalate, $BaC_2O_4$, soluble in acids, including $HC_2H_3O_2$.

4. $K_2CrO_4$ precipitates yellow barium chromate, $BaCrO_4$, soluble in HCl and $HNO_3$; somewhat soluble in $HC_2H_3O_2$ and in $NH_4Cl$; insoluble in potassium dichromate, $K_2Cr_2O_7$, which latter salt is formed by the action of acids on $K_2CrO_4$ : —

$$2 K_2CrO_4 + 2 HCl = K_2Cr_2O_7 + 2 KCl + H_2O.$$

Hence, in acid solutions of barium salts, $K_2CrO_4$ should be added in excess to neutralize the acids.

5. **Ether-alcohol** does not dissolve barium nitrate, $Ba(NO_3)_2$. As $Ba(NO_3)_2$ is soluble in water, it is necessary to conduct the experiment with a perfectly dry salt.

6. **Heated** on a platinum wire in the flame of the Bunsen lamp, barium salts give a yellow-green color, which, seen through a cobalt glass, appears blue-green.

7. **Spectrum** (see Table VII, p. 58).

## Strontium (salt for study, strontium nitrate, $Sr(NO_3)_2$).

1. **$(NH_4)_2CO_3$** precipitates white strontium carbonate, $SrCO_3$, which for the most part behaves towards reagents like $BaCO_3$. It is less soluble in $NH_4Cl$ than $BaCO_3$.

2. **$H_2SO_4$** (also $CaSO_4$) precipitates white strontium sulphate, $SrSO_4$, sparingly soluble in water, but more soluble in HCl and $HNO_3$; insoluble in $(NH_4)_2SO_4$.

3. **$(NH_4)_2C_2O_4$** gives a reaction similar to 3, under barium, except that $SrC_2O_4$ is almost insoluble in $HC_2H_3O_2$.

4. **$K_2CrO_4$** does not precipitate yellow strontium chromate, $SrCrO_4$, except on long-standing and in concentrated neutral solutions. $SrCrO_4$ is quite soluble in $HC_2H_3O_2$.

5. **Ether-alcohol** does not dissolve strontium nitrate, $Sr(NO_3)_2$, but as it is very soluble in water, it is essential to conduct the experiment with a freshly heated anhydrous salt.

6. **Heated** in a non-luminous flame on a platinum wire, strontium salts give a deep red color, which, seen through a blue glass, appears blue.

7. **Spectrum** (see Table VII, p. 58).

### Calcium (salt for study, calcium nitrate, $Ca(NO_3)_2$).

1. $(NH_4)_2CO_3$ gives a reaction similar to 1, under barium, except that $CaCO_3$ is more soluble than $BaCO_3$ in $NH_4Cl$ and in $H_2SO_4$.

2. $H_2SO_4$ precipitates white calcium sulphate, $CaSO_4$, sparingly soluble in water and acids; insoluble in alcohol. In this latter experiment it is necessary that the calcium salt be in a concentrated solution.

3. $(NH_4)_2C_2O_4$ precipitates white calcium oxalate, soluble in strong acid; insoluble in $HC_2H_3O_2$.

4. $K_2CrO_4$ gives no precipitate if the solution is acidified with $HC_2H_3O_2$.

5. **Ether-alcohol** dissolves calcium nitrate, $Ca(NO_3)_2$.

6. **Heated** in a non-luminous flame on a platinum wire, calcium salts give a pale red color, which appears green-gray if seen through a blue glass.

7. **Spectrum** (see Table VII, p. 58).

#### PROCESS OF SEPARATION

The separation of the members of this group may be made by three methods, which are based on the following phenomena: —

*Method 1.*   (*a*) Insolubility of $Ba(NO_3)_2$ and $Sr(NO_3)_2$ in ether-alcohol;

           (*b*) Insolubility of $BaCrO_4$ in $K_2Cr_2O_7$ solution.

*Method 2.*    (a)  Insolubility of $BaCrO_4$ in $K_2Cr_2O_7$ solu-
                    tion ;

              (b)  Insolubility of $SrSO_4$ in $(NH_4)_2SO_4$ solu-
                   tion.

*Method 3.*    Differences between the spectra of barium,
              strontium, and calcium salts.

The solution is first made alkaline with $NH_4OH$, $NH_4Cl$ is added in moderate quantity, and finally $(NH_4)_2CO_3$ solution is added till the precipitation is completed. The mixture should be warmed (not boiled), filtered, and washed with ammoniated water. The filtrate (a) may contain members of Group VI. The residue (a) may consist of $BaCO_3$, $SrCO_3$, and $CaCO_3$.

*Method 1.* — Dissolve the residue (a) in an evaporating dish with a minimum of dilute $HNO_3$, and evaporate carefully to dryness. Remove to an iron plate (a small clean sand bath may be used) and heat to dull redness, till all traces of moisture are expelled, tested by holding a cold *dry* watch-glass or beaker over the dish. After cooling, quickly triturate the mass in a dry mortar with about 10 c.c. ether-alcohol. Transfer to a small dry flask and shake the corked flask at intervals. After about an hour filter through a dry paper (filtrate (b)) and wash the residue (b) with a little ether-alcohol till the drippings show no cloudiness with dilute $H_2SO_4$. Dissolve the residue (b), possibly consisting of $Ba(NO_3)_2$ and $Sr(NO_3)_2$, in warm water acidified with a few drops of $HC_2H_3O_2$, and while boiling add $K_2CrO_4$ till the solution ceases to smell of $HC_2H_3O_2$. A yellow precipitate confirms $BaCrO_4$. Filter, and to the filtrate (c) add $NH_4OH$ and $(NH_4)_2CO_3$. A white precipitate confirms $SrCO_3$. To the filtrate (b) add

some dilute $H_2SO_4$. A white precipitate confirms $CaSO_4$.

In the separation of the nitrates of the group with ether-alcohol, not only the external moisture but also the water of crystallization of the nitrates must be expelled. The temperature may reach 180° and not injure the salts, but above that degree the nitrates are dissociated into the insoluble oxides.

*Method 2.* —Dissolve the residue (*a*) in a small amount of dilute $HC_2H_3O_2$ and add $K_2CrO_4$ till the solution ceases to smell of $HC_2H_3O_2$. A yellow precipitate, residue (*b*), confirms $BaCrO_4$. Filter. Add to the filtrate (*b*) a concentrated solution of $(NH_4)_2SO_4$, and boil. Filter. The residue (*c*) indicates $SrSO_4$, which can be confirmed with the flame. Add to the filtrate (*c*) some $(NH_4)_2C_2O_4$. A white precipitate confirms $CaC_2O_4$.

*Method 3.* — Dissolve the residue (*a*) in the least possible amount of HCl and evaporate to a thin paste. Test with the spectroscope for barium, strontium, and calcium.

Magnesium, in many respects, behaves like the three other alkali-earth metals — barium, strontium, and calcium. In one respect, however, magnesium differs very materially from the other kindred metals. Its salts readily dissolve in ammonium salts, but only to a very limited degree do ammonium salts affect the solubility of the salts of barium, strontium, and calcium. Hence $NH_4Cl$ must be added with $(NH_4)_2CO_3$ to prevent the precipitation of $MgCO_3$, but an excess of the reagent must be avoided lest it also dissolve the other carbonates. Heating is usually conducive to precipitation ; but in this case great heat dissociates $(NH_4)_2CO_3$ into $NH_3$ and $H(NH_4)_2CO_3$, which latter acid salt, being poorly ionized, does not precipitate the carbonates of the group. Hence the solution must be warmed, but not boiled.

# CHAPTER XII

## METALS OF GROUP VI: MAGNESIUM, AMMONIUM, POTASSIUM, AND SODIUM

**No group characteristic. No group reagent.**

### REACTIONS

## Magnesium (salt for study, magnesium chloride, $MgCl_2$).

1. **$HNa_2PO_4$** precipitates white crystalline acid magnesium phosphate, $HMgPO_4$, very soluble in acids; somewhat soluble in water. If $NH_4Cl$ and $NH_4OH$ are added before $HNa_2PO_4$, the more insoluble $(NH_4)MgPO_4$ will be precipitated. It is soluble in acids, even $HC_2H_3O_2$. Precipitation is hastened by rubbing the side of the vessel with a glass rod.

2. **$NH_4OH$** and **NaOH** precipitate white magnesium hydroxide, $Mg(OH)_2$, soluble in acids and in $NH_4Cl$.

3. **Spectrum** (see Table VII, p. 58).

## Ammonium (salt for study, ammonium chloride, $NH_4Cl$).

1. **$H_2PtCl_6$**[1] in neutral or acid solutions precipitates yellow crystalline ammonium platinic chloride, $(NH_4)_2PtCl_6$, insoluble in alcohol; sparingly soluble in water and dilute acids. As the salt is somewhat soluble in water, it is best to add $H_2PtCl_6$, evaporate nearly to dryness, and add a few drops of alcohol.

2. **$H_2C_4H_4O_6$** in neutral concentrated solutions precipitates white acid ammonium tartrate, $H(NH_4)C_4H_4O_6$,

insoluble in alcohol; somewhat soluble in water; soluble in acids. The reagent should be added like $H_2PtCl_6$.

3. **NaOH** sets free $NH_3$, detected by the odor, with red litmus paper, or with a glass rod moistened with concentrated HCl.

4. **Heated** on a platinum foil, all ammonium salts are completely volatilized.

### Potassium (salt for study, potassium chloride, KCl).

1. $H_2PtCl_6$ gives a reaction very similar to 1, under ammonium.

2. $H_2C_4H_4O_6$ gives a reaction very similar to 2, under ammonium.

3. **Heated** in a non-luminous flame, potassium salts color the flame violet, which appears purple when seen through a blue glass.

4. **Spectrum** (see Table VII, p. 58).

### Sodium (salt for study, sodium chloride, NaCl).

1. $H_2K_2Sb_2O_7$ in concentrated neutral solutions precipitates sodium pyro-antimoniate, $H_2Na_2Sb_2O_7$.

2. **Heated** in a non-luminous flame, sodium salts color the flame yellow, which color cannot be seen through a blue glass.

3. **Spectrum** (see Table VII, p. 58).

#### PROCESS OF SEPARATION

As the group is composed of metals not bound by a common group reagent, and as salts of some of the

metals may have been used as reagents in previous groups, the detection of the individuals cannot be made entirely by separations, but in part by separations and in part by individual tests in the original solutions.

The detection of the members of this group is based upon the facts that $NH_4MgPO_4$ is insoluble in presence of $NH_4OH$ and $NH_4Cl$; that $K_2PtCl_6$ and $NH_4PtCl_6$ are insoluble in alcohol solutions; and that ammonium salts are dissociated by strong alkalies, and completely volatilized by strong heat.

Concentrate the solution by evaporation. Divide the solution into two unequal parts.

*First Part (smaller).* — Add $NH_4OH$, $NH_4Cl$, and $HNa_2PO_4$. A white crystalline precipitate appearing immediately or after some time confirms $NH_4MgPO_4$.

The precipitate should be crystalline, and if the sides of the vessel are scratched with a glass rod the crystals will adhere to the vessel in clusters in the path of the scratching. As the crystalline structure of the precipitate is distinctly characteristic of $NH_4MgPO_4$, it is often desirable to confirm this with the microscope. A simple method is to allow the crystals to grow for several hours. Then carefully decant off the liquid, and examine the sides of the glass vessel with a reading glass or simple microscope. If the precipitate appears flocculent and crystals cannot be detected, examine it for $Al(OH)_3$ with the spectroscope. $Al(OH)_3$ can possibly appear at this stage of the separation because it is soluble in excess of $NH_4OH$, and may have been brought over from Group III.

*Second Part (larger).* — Evaporate to dryness and expel ammonium salts by removing the mass from the dish, and heating on a platinum foil till no white fumes appear immediately after removal from the flame.

Moisten the residue with HCl and test for potassium and sodium with the simple flame and with the spectroscope. Confirm the test for potassium by adding to the moistened residue some $H_2PtCl_6$ and alcohol.

Both ammonium and potassium salts give very similar precipitates with $H_2PtCl_6$; hence it is necessary to remove all the ammonium salts by sublimation. Care should be taken not to heat the substance too much, as potassium chloride is also somewhat volatile and might be lost.

As ammonium salts are used as reagents in several groups, it is obviously necessary to test for ammonia in the original solution.

Concentrate some of the original solution and test with NaOH for ammonium salts.

## CHAPTER XIII

### ACIDS OF GROUP I: CHROMIC, CARBONIC, SILICIC, SULPHUROUS, SULPHURIC, PHOSPHORIC, BORIC, OXALIC, TARTARIC, AND HYDROFLUORIC ACIDS

CHARACTERISTIC: **Insolubility of their barium salts in neutral solution.**

GROUP REAGENT: **Barium chloride.**

#### REACTIONS

### Chromic Acid, $H_2CrO_4$ (salt for study, potassium chromate, $K_2CrO_4$).

1. **$BaCl_2$** precipitates yellow barium chromate, $BaCrO_4$, soluble in dilute acids, except $H_2SO_4$.

2. **$H_2S$** reduces $CrO_3$ to $Cr_2O_3$; so that Cr will be detected in the analysis for the metals, even though it originally were present in its acid state of oxidation.

3. **$Pb(C_2H_3O_2)_2$** precipitates yellow lead chromate, — chrome yellow, — insoluble in $HC_2H_3O_2$.

(For other reactions, see Chromium as a metal.)

### Carbonic Acid, $H_2CO_3$ (salt for study, sodium carbonate, $Na_2CO_3$).

1. **$BaCl_2$** precipitates white barium carbonate, $BaCO_3$, insoluble in water; soluble in acids, except $H_2SO_4$. This reaction occurs only with salts of $H_2CO_3$, not with the free acid.

2. **HCl** and other acids, excepting $H_2S$ and HCN, decompose carbonates with evolution of $CO_2$. This gas is readily soluble in water; and in dilute solutions of the carbonates, it may not be formed in sufficient quantity to oversaturate the solution and escape. From concentrated or hot solutions, it escapes with effervescence. Being heavier than air, it may be detected by decantation into a test-tube containing lime water, its presence being shown by the appearance of a milky precipitate : —

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O.$$
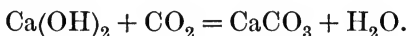
An excess of $CO_2$ will dissolve the precipitate first formed. Sulphur dioxide, $SO_2$, will also produce a white precipitate with lime water, but can usually be detected by its odor.

### Silicic Acid, $H_4SiO_4$ (salt for study, sodium silicate, $Na_4SiO_4$).

1. **BaCl₂** precipitates white barium silicate, $Ba_2SiO_4$, decomposed by dilute HCl, with separation of gelatinous $H_4SiO_4$.

2. **HCl** added, drop by drop, to the solution of a silicate, precipitates gelatinous $H_4SiO_4$, which, on evaporation to dryness, is decomposed with the formation of silicic anhydride, $SiO_2$.

3. **Fused** with $Na_2CO_3$ on a platinum foil until bubbles of gas cease to escape, most insoluble silicates are changed by metathesis to sodium silicate and a metallic carbonate or oxide. If the fused mass is then boiled with dilute HCl and filtered, the filtrate will contain

the chloride of the metal and the residue will consist of $H_4SiO_4$ : —

    (*a*)  $Ba_2SiO_4 + 2Na_2CO_3 = 2BaCO_3 + Na_4SiO_4$ ;
    (*b*)  $BaCO_3 + 2HCl = BaCl_2 + H_2O + CO_2$ ;
    (*c*)  $Na_4SiO_4 + 4HCl = H_4SiO_4 + 4NaCl$.
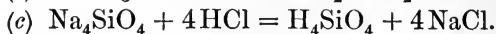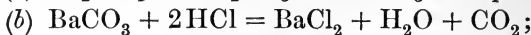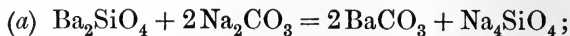
4. **HF** in an aqueous solution, or in gaseous form, decomposes $SiO_2$ with evolution of silicon tetrafluoride, $SiF_4$ : —

$$SiO_2 + 4HF = SiF_4 + 2H_2O.$$
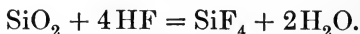
If a silicate is mixed with three parts of $NH_4F$ or five parts of $CaF_2$, moistened with concentrated $H_2SO_4$, and then heated till fumes cease to escape, the silicic acid is decomposed and expelled : —

    (*a*)  $H_2SO_4 + 2NH_4F = (NH_4)_2SO_4 + 2HF$ ;
    (*b*)  $6HF + Na_2SiO_3 = Na_2SiF_6 + 3H_2O$ ;
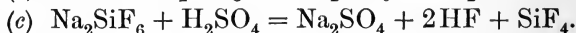    (*c*)  $Na_2SiF_6 + H_2SO_4 = Na_2SO_4 + 2HF + SiF_4$.
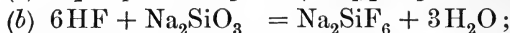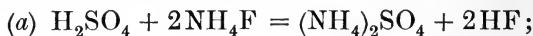
5. **Metaphosphate bead** dissolves the metallic parts of the silicates, but not the $SiO_2$, which remains floating in the fused bead. As $SiO_2$ is not affected, the outline of the particle of the silicate remains intact, giving rise to the so-called " skeleton bead."

### ANALYSIS OF SILICATES

There are two classes of silicates important in analytical chemistry — silicates decomposed by acids, and those not decomposed by acids : —

First class: Silicates decomposed by acids. This is not a very numerous class, composed for the most part of the soluble alkali metal silicates and a few less soluble single and double silicates of other metals. The analysis of this class is quite simple. This

is accomplished by treatment of the silicates with HCl, which by metathesis form soluble chlorides of the metals and colloidal silicic acid.

Second class: Silicates not decomposed by acids. This constitutes by far the more numerous class, including the natural silicates. Many natural silicates contain the alkali metals combined with other metals. The varieties of feldspar are representatives of this kind.

The analysis of silicates not decomposed by acids is usually conducted by one of three methods: —

*Method 1.*—Fusion with alkali-metal carbonates. By metathesis, soluble silicates and carbonates of the metals of the original silicates are formed, — which resulting salts are then decomposed by HCl (see reactions above). Finely powder the silicate, mix with about 3 parts of $Na_2CO_3$, or fusion mixture, and heat to quiet fusion in a platinum crucible or foil. When cool, boil the mass in water. Filter, evaporate to a small bulk, and add concentrated HCl. $H_2SiO_3$ will precipitate as a gelatinous mass. If it is desired to test for the presence of alkali metals in the silicate, this method cannot be used, as the carbonates of these metals are added as a flux.

*Method 2.*[1]—(Method of J. Lawrence Smith.) Fusion with $NH_4Cl$ and $CaCO_3$. An insoluble silicate like feldspar, containing alkali metals, may be converted into soluble alkali-metal chlorides and some insoluble hydroxides, by heating to redness in a covered platinum crucible with 1 part $NH_4Cl$ and 8 parts powdered $CaCO_3$. In all fusions it is necessary for both the substance and the flux to be reduced to very fine powders, and intimately mixed.

*Method 3.* — Fusion with BaO. Fuse in a platinum crucible a mixture of 1 part of the powdered silicate and 4 parts BaO. Digest the mass in a little water to detach it from the crucible, and then dissolve in HCl. Add $NH_4OH$ till alkaline, filter, evaporate to dryness, and ignite.

### Sulphurous Acid, $H_2SO_3$ (salt for study, sodium sulphite, $Na_2SO_3$).

1. **BaCl₂** precipitates white barium sulphite, $BaSO_3$, soluble in dilute HCl.

2. **Nascent hydrogen** reduces sulphites to sulphides, which are decomposed by an excess of HCl with evolution of $H_2S$, detected by its odor, or with $Pb(C_2H_3O_2)_2$.

3. **H₂S** decomposes sulphites with separation of sulphur.

4. **HCl** decomposes sulphites with evolution of $SO_2$, detected by its odor and by the production of a white precipitate of calcium sulphite with lime water.

### Sulphuric Acid, $H_2SO_4$ (salt for study, sodium sulphate, $Na_2SO_4$).

1. **BaCl₂** precipitates white barium sulphate, $BaSO_4$, insoluble in water or acids; decomposed by fusion with $Na_2CO_3$ in a platinum crucible or foil, sodium sulphate and barium carbonate being formed : —

$$Na_2CO_3 + BaSO_4 = Na_2SO_4 + BaCO_3.$$
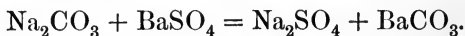
In like manner, the other insoluble sulphates, $SrSO_4$, $CaSO_4$, and $PbSO_4$, are decomposed by fusion with $Na_2CO_3$ or by boiling with its solution.

2. **Pb(C₂H₃O₂)₂** precipitates white lead sulphate, $PbSO_4$, almost insoluble in dilute $HNO_3$ ; soluble in hot concentrated HCl.

3. **Fused** with $Na_2CO_3$ on charcoal, sulphates are reduced to sulphides. If the mass is moistened with very dilute HCl and placed on a bright silver coin, the latter will be stained black.

## Phosphoric Acid, $H_3PO_4$ (salt for analysis, sodium phosphate, $HNa_2PO_4$).

1. **$BaCl_2$** precipitates white barium phosphate, $HBaPO_4$, — or $Ba_3(PO_4)_2$, if the solution contained a normal phosphate, — soluble in HCl and $HNO_3$.

2. **$MgSO_4$** in presence of $NH_4OH$ and $NH_4Cl$ precipitates white crystalline ammonium magnesium phosphate, $NH_4MgPO_4$, soluble in acids. (Compare with $NH_4MgAsO_4$.)

3. **$(NH_4)_2MoO_4$** in $HNO_3$ solution precipitates, in the cold, yellow ammonium phospho-molybdate, $(MoO_3)_{12} \cdot (NH_4)_3PO_4$. (Compare with behavior of the same reagent toward arsenates.)

4. **$FeCl_3$** in presence of $NaC_2H_3O_2$ precipitates yellow ferric phosphate, $FePO_4$, soluble in strong acids and excess of $FeCl_3$; insoluble in $HC_2H_3O_2$.

## Boric Acid, $H_3BO_3$ (salt for study, borax, $Na_2B_4O_7$).

1. **$BaCl_2$** precipitates white sodium barium borate, $Na_2Ba_5(BO_3)_4$, soluble in acids, except $H_2SO_4$.

2. **$H_2SO_4$** precipitates from hot solutions of borates, on cooling, crystalline boric acid, $H_3BO_3$.

3. **Alcohol**, added to free boric acid or to a borate with concentrated $H_2SO_4$ and then kindled, burns with a green flame, especially upon stirring the mixture.

4. **Turmeric paper**, immersed in a slightly acid (HCl) solution of boric acid or a borate and then dried, shows a reddish tint which is turned blue by NaOH.

## Oxalic Acid, $H_2C_2O_4$ (salt for study, sodium oxalate, $Na_2C_2O_4$).

1. $BaCl_2$ precipitates from neutral solutions white barium oxalate, $BaC_2O_4$, somewhat soluble in dilute $NH_4Cl$ and many organic acids; soluble in HCl and $HNO_3$.

2. Lime water and soluble calcium salts precipitate white calcium oxalate $CaC_2O_4$, soluble in HCl and $HNO_3$; insoluble in organic acids.

3. Concentrated $H_2SO_4$, heated with oxalic acid or an oxalate, removes water, and the compound is decomposed into $CO_2$ and CO : —

$$H_2C_2O_4 + H_2SO_4 = CO_2 + CO + H_2SO_4 \cdot H_2O.$$
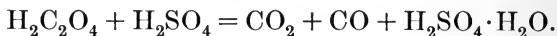
If in sufficient quantity the CO gas can be burned with its characteristic blue flame.

4. Heating decomposes all oxalates with formation of carbonates or oxides of the metals, and evolution of CO or $CO_2$.

## Tartaric Acid, $H_2C_4H_4O_6$ (salt for study, potassium tartrate, $K_2C_4H_4O_6$).

1. $BaCl_2$ (or, better, $CaCl_2$) from neutral solutions precipitates white barium (or calcium) tartrate, soluble in acids, except $H_2SO_4$.

2. $AgNO_3$ precipitates white silver tartrate, $Ag_2C_4H_4O_6$, soluble in $NH_4OH$. On warming this solution, black metallic silver is deposited. If the $Ag_2C_4H_4O_6$ be carefully redissolved in the least possible amount of $NH_4OH$, and if this solution be heated gently

in a test-tube, a mirror of metallic silver will be deposited on the walls of the tube. $AgNO_3$ precipitates $Ag_2C_4H_4O_6$ only from neutral solutions. This reaction distinguishes tartaric from most other organic acids.

3. **Heated** in a closed tube, tartrates char and emit inflammable vapors with the odor of burnt sugar. Commingled with the carbon residue is also a carbonate, detected by effervescence on adding HCl.

## Hydrofluoric Acid, HF (salt for study, ammonium fluoride, $NH_4F$).

1. **BaCl$_2$** precipitates white barium fluoride, $BaF_2$, soluble with difficulty in HCl and $HNO_3$.

2. **Concentrated H$_2$SO$_4$** mixed to a paste with powdered fluorides and warmed in a platinum vessel expels gaseous HF : —

$$2NH_4F + H_2SO_4 = (NH_4)_2SO_4 + 2HF.$$
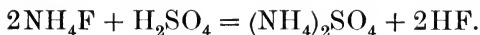
If the vessel is loosely covered for an hour with a watch-glass which previously has been coated with wax through which some lines have been cut with a sharp instrument, the lines will be seen to have been etched into the glass upon removal of the wax. The reaction involved is identical with No. 4, under silicic acid.

### DETECTION OF THE ACIDS OF GROUP I

The analysis for acids cannot be made by following a systematic scheme of separation, such as is used in the analysis for metals; on the contrary, the presence or absence of each acid must be established chiefly by individual tests applied to the original material.

For convenience the members of Group I may be classified as follows : —

*Sub-group I —* $H_2CrO_4$, $H_2CO_3$, $H_4SiO_4$, $H_2SO_3$. These acids are decomposed, in solution, by HCl and $H_2S$.

*Sub-group II —* $H_2SO_4$, $H_3PO_4$, $H_3BO_3$, $H_2C_2O_4$, $H_2C_4H_4O_6$, HF. These acids are not decomposed by HCl or $H_2S$.

Neutralize a small portion of the original solution, and add some $BaCl_2$ (or $Ba(NO_3)_2$, if metals of Group I are present). A precipitate confirms the presence of one or more acids of Group I. Divide a larger portion of the original solution into four parts : —

*Part I, for chromic acid.* — A yellow color indicates chromic acid, confirmed by acidifying with $HC_2H_3O_2$ and adding $Pb(C_2H_3O_2)_2$.

*Part II, for carbonic acid.* — Add HCl and warm. An effervescence of an odorless gas indicates the presence of $CO_2$. Confirm by testing with lime water.

*Part III, for sulphurous acid.* — Add HCl and warm. Effervescence with odor of burning sulphur indicates the presence of $SO_2$, confirmed by passing the gas through lime water.

*Part IV, for silicic acid.* — Add dilute HCl, drop by drop. A gelatinous precipitate indicates $H_4SiO_4$, confirmed by evaporating to dryness and testing with the metaphosphate bead.

If any of these acids are present, they must be removed from solution before testing for the members of Sub-group II. $H_2CrO_4$ is destroyed by $H_2S$, in

presence of HCl; $H_2CO_3$ and $H_2SO_3$ are driven off by boiling with HCl; and $H_4SiO_4$ is removed by evaporation with HCl.

The solution, thus freed of members of Sub-group I, is now neutralized exactly with $NH_4OH$, — free of $(NH_4)_2CO_3$, — and its examination is continued as follows : —

To a small portion $BaCl_2$ is added. If no precipitate is formed, all members of Sub-group II are absent. If a precipitate is formed which dissolves on the addition of HCl, $H_2SO_4$ is absent, but other members may be present. If a precipitate is formed which does not dissolve in HCl, $H_2SO_4$ (possibly other acids) is present. In either of the latter cases it is necessary to test individually for the remaining acids of the group in small portions of the solution.

*Part I, for phosphoric acid.* — Add a few drops of the solution to a strong $HNO_3$ solution of $(NH_4)_2MoO_4$, and warm gently. A yellow crystalline precipitate confirms the presence of $H_3PO_4$.

*Part II, for boric acid.* — Acidify some of the solution with HCl and test with turmeric paper. Evaporate another portion almost to dryness, add alcohol and concentrated $H_2SO_4$, and kindle. A green flame confirms the presence of $H_3BO_3$.

*Part III, for oxalic acid.* — Add lime water and boil the white precipitate with $HC_2H_3O_2$. If the precipitate fails to dissolve, it confirms the presence of $H_2C_2O_4$.

*Part IV, for tartaric acid.* — Neutralize the solution and add $CaCl_2$. If a white precipitate occurs, filter, dry the residue, and heat in a closed tube. Charring with

the odor of burnt sugar, and effervescence of the residue with HCl, confirm the presence of $H_2C_4H_4O_6$.

*Part V, for hydrofluoric acid.*—Evaporate the solution to dryness, transfer the residue to a platinum crucible, add concentrated $H_2SO_4$, and cover with a watch-glass. If the gas etches the glass cover, the presence of HF is confirmed.

# CHAPTER XIV

## ACIDS OF GROUP II: HYDROCHLORIC, HYDROBROMIC, HYDRIODIC, HYDROCYANIC, HYDROFERROCYANIC, HYDROFERRICYANIC, SULPHOCYANIC, AND HYDRO-SULPHURIC ACIDS

CHARACTERISTIC: **Insolubility of their silver salts in dilute nitric acid.**

GROUP REAGENT: **Silver nitrate.**

### REACTIONS

## Hydrochloric Acid, HCl (salt for study, sodium chloride, NaCl).

1. **AgNO$_3$** precipitates white silver chloride, AgCl, insoluble in dilute acids; soluble in KCN, NH$_4$OH, and in boiling solution of ammonium "sesqui" carbonate.

2. **PbO$_2$** or **MnO$_2$** with concentrated H$_2$SO$_4$ expels chlorine gas, detected with starch-KI paper.

3. **K$_2$Cr$_2$O$_7$** with concentrated H$_2$SO$_4$ gives red fumes, condensing to a brown liquid, chromic oxychloride, CrO$_2$Cl$_2$, changing to yellow (NH$_4$)$_2$CrO$_4$ on the addition of NH$_4$OH. The dry chloride should be triturated with K$_2$Cr$_2$O$_7$ crystals, and distilled with concentrated H$_2$SO$_4$ in a small retort (25 c.c.).

### Hydrobromic Acid, HBr (salt for study, potassium bromide, KBr).

1. $AgNO_3$ precipitates yellow silver bromide, AgBr, insoluble in dilute acids and in ammonium "sesqui" carbonate; soluble in $NH_4OH$ and KCN.

2. $PbO_2$ with concentrated $H_2SO_4$ expels brown vapors of bromine, identified by their odor and color.

3. $K_2Cr_2O_7$ with concentrated $H_2SO_4$ expels bromine, which is decolorized by $NH_4OH$, forming $NH_4Br$.

4. Chlorine liberates bromine, detected in small quantities by coloring carbon disulphide or chloroform brownish-red. Mix the bromide solution with about 1 c.c. of $CS_2$, then add dilute chlorine water, drop by drop, and shake well. The globules of $CS_2$ will assume a reddish tint. An excess of chlorine should be avoided, lest it combine with bromine to form colorless bromine chloride, BrCl.

### Hydriodic Acid, HI (salt for study, potassium iodide, KI).

1. $AgNO_3$ precipitates yellow silver iodide, AgI, insoluble in dilute acids, $NH_4OH$ and ammonium "sesqui" carbonate; soluble in KCN.

2. $PbO_2$ with concentrated $HC_2H_3O_2$ liberates violet iodine, turning starch paper blue.

3. $K_2Cr_2O_7$ with concentrated $H_2SO_4$ liberates iodine.

4. Chlorine water liberates iodine, turning starch paper blue. An excess of chlorine will decolorize the paper by formation of iodine chloride, ICl.

5. $KNO_2$ in concentrated $H_2SO_4$ liberates iodine. Into a clear solution of starch paste and an iodide, dip

a glass rod moistened with a solution of $KNO_2$ in concentrated $H_2SO_4$. The liquid in contact with the rod becomes blue. It is necessary to keep the reagent cold, as iodized starch becomes colorless in hot water.

## Hydrocyanic Acid, HCN (salt for study, potassium cyanide, KCN).

1. **AgNO₃** precipitates white silver cyanide, AgCN, soluble in excess of KCN, forming the salt $KAg(CN)_2$. AgCN is also soluble in $NH_4OH$ and boiling HCl.

2. **FeSO₄**, with a few drops of $FeCl_3$, added to the solution of a cyanide in weak NaOH, precipitates a bluish-green mixture of ferrous ferric hydroxide, $Fe_3O_2(OH)_4$, and Prussian blue. $Fe_3O_2(OH)_4$ can be dissolved with dilute HCl, leaving the Prussian blue intact.

3. **(NH₄)₂Sₓ**(a few drops) and a drop of NaOH added to a cyanide solution, form ammonium sulphocyanate, $NH_4CNS$, on heating. Evaporate the solution to dryness and test by dissolving in dilute HCl and adding $FeCl_3$ solution. A deep red coloration shows the presence of HCNS, derived from HCN : —

$$(NH_4)_2S_x + 4\,KCN = 4\,KCNS + (NH_4)_2S(x-4).$$

4. **HNaCO₃** heated with a cyanide expels HCN gas, identified by its odor and the rose color of its flame.

## Hydroferrocyanic Acid, $H_4Fe(CN)_6$ (salt for study, potassium ferrocyanide, $K_4Fe(CN)_6$).

1. **AgNO₃** precipitates white silver ferrocyanide, $Ag_4Fe(CN)_6$, soluble in KCN; insoluble in $NH_4OH$ and $HNO_3$.

2. $FeCl_3$ precipitates Prussian blue (see Iron, p. 107).

3. $CuSO_4$ precipitates brown cupric ferrocyanide, $Cu_2Fe(CN)_6$ (see Copper, p. 84).

## Hydroferricyanic Acid, $H_3Fe(CN)_6$ (salt for study, potassium ferricyanide, $K_3Fe(CN)_6$).

1. $AgNO_3$ precipitates orange-red silver ferricyanide, $Ag_3Fe(CN)_6$, soluble in $NH_4OH$ and $KCN$; insoluble in $HNO_3$.

2. $FeSO_4$ precipitates Turnbull's blue (see Iron, p. 107).

## Sulphocyanic Acid, HCNS (salt for study, potassium sulphocyanate, KCNS).

1. $AgNO_3$ precipitates white silver sulphocyanide, $AgCNS$, soluble in $NH_4OH$; insoluble in dilute $HNO_3$.

2. $FeCl_3$ acidified with HCl gives a deep red coloration of $Fe(CNS)_3$ (see Iron, p. 108).

## Hydrosulphuric Acid, $H_2S$ (salt for study, sodium sulphide, $Na_2S$).

1. $AgNO_3$ precipitates black silver sulphide, $Ag_2S$.

2. $Na_2FeNO(CN)_5$ (sodium nitro-prusside) added to alkaline (NaOH) solution of a sulphide gives a brilliant red-violet tint.

3. Fused with NaOH, insoluble sulphides form $Na_2S$; and on dissolving the mass in a little water, the solution will tarnish a bright silver coin brown.

4. HCl sets free $H_2S$ from all soluble, and from many insoluble sulphides; recognized by its odor and by its

power of blackening paper moistened with a solution of $Pb(C_2H_3O_2)_2$.

## DETECTION OF THE ACIDS OF GROUP II

The separation and identification of the acids of this group are accomplished by the following means: —

(*a*) The removal of $H_2S$ by means of a solution of $ZnSO_4$ in NaOH.

(*b*) Hager's method of detecting HCl, HBr, and HI in the presence of each other; based upon the different degrees of solubility of AgCl, AgBr, and AgI in ammonium "sesqui" carbonate and $NH_4OH$.

(*c*) The detection of HCN in the absence of $H_4Fe(CN)_6$, $H_3Fe(CN)_6$, and HCNS, by the precipitation of Prussian blue from a solution of a cyanide by $FeSO_4$, $FeCl_3$, and NaOH.

(*d*) The detection of HCN in the presence of $H_4Fe(CN)_6$, $H_3Fe(CN)_6$, and HCNS, by the evolution of HCN on distilling with $HNaCO_3$.

$H_2S$ must first be tested for in a small portion of the original solution, preferably by adding HCl, boiling, and noting whether any gas is given off which causes lead acetate paper to blacken. If found, it must be removed from the remainder of the solution before testing for the other members of the group, since its presence would hinder their detection. Therefore, treat a sufficient portion of the solution with a solution of $ZnSO_4$ in an excess of NaOH, which will precipitate the $H_2S$ as ZnS. Reject the precipitate, and divide the filtrate, or portion of the original solution if $H_2S$ is absent, into three parts.

*Part I, for HCl, HBr, and HI.*[1]—Acidify with $HNO_3$ and add $AgNO_3$. Filter and reject the filtrate. Boil the residue with 100 parts of a solution of ammonium "sesqui" carbonate. Decant the clear supernatant liquid, add more ammonium "sesqui" carbonate, and again boil and decant. The decanted liquid may contain AgCl, which can be determined by acidifying with $HNO_3$. The residue from which the liquid has been decanted may consist of AgBr and AgI. Treat it with a dilute solution of $NH_4OH$ (5 per cent ammonia water) and filter. The filtrate may contain AgBr, detected by acidifying with $HNO_3$. The residue may be AgI, indicated by its yellow color. For a further confirmation of the three halogens (consisting of the AgCl and AgBr precipitates from the ammoniacal solutions and the undissolved AgI) each can be fused with $Na_2CO_3$, boiled with water, and filtered:—

$$2\,AgCl + Na_2CO_3 = 2\,NaCl + Ag_2CO_3, \text{ etc.}$$
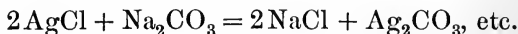
The filtrates can be tested for the individual halogens as follows:—

(*a*) Solution of NaCl. Evaporate to dryness and heat with concentrated $H_2SO_4$ and $PbO_2$. The evolved chlorine can be detected by its odor, its bleaching moistened litmus paper, or its effect on starch-KI paper.

(*b*) Solution of NaBr. Evaporate to dryness and heat with concentrated $H_2SO_4$ and $PbO_2$. The evolved bromine can be detected by its odor or by its color.

(*c*) Solution of NaI. Neutralize with $HNO_3$ and add some drops of starch paste and chlorine water. A blue solution confirms presence of the iodide.

*Part II, for $H_4Fe(CN)_6$, $H_3Fe(CN)_6$, and HCNS.* —
Neutralize with $HNO_3$ and divide into two small parts.
Pour one part into a test-tube and shake the tube so
that its sides will be moistened with the liquid. Hold-
ing the tube obliquely, add a few drops of dilute $FeCl_3$
solution so that they will run down the sides of the
tube. A red coloration indicates the presence of HCNS.
If $H_4Fe(CN)_6$ is present, Prussian blue will be formed
also, but the red color can be seen commingled with the
blue. Add more $FeCl_3$. The formation of Prussian
blue confirms presence of $H_4Fe(CN)_6$. To the second
smaller part add $FeSO_4$. The formation of Turnbull's
blue confirms the presence of $H_3Fe(CN)_6$.

*Part III, for HCN.* — If $H_4Fe(CN)_6$, $H_3Fe(CN)_6$,
and HCNS are absent, add NaOH, $FeSO_4$, a few drops
of $FeCl_3$, and HCl in excess. Formation of Prussian
blue confirms the presence of HCN.

If $H_4Fe(CN)_6$, $H_3Fe(CN)_6$, and HCNS are present,
add some solid bicarbonate of sodium, $HNaCO_3$, to the
neutral solution in a test-tube, and boil. The odor of
bitter almonds indicates the presence of HCN. Con-
firm by kindling the gas. It should burn with a rose-
tinted flame.

*HCN is a deadly poison ; do not inhale.*

# CHAPTER XV

## ACIDS OF GROUP III: NITRIC, CHLORIC, AND ACETIC ACIDS

### No group characteristic.  No group reagent.

#### REACTIONS

### Nitric Acid, $HNO_3$ (salt for study, potassium nitrate, $KNO_3$).

1. **Heated** on charcoal, nitrates deflagrate with ignition, giving off $CO_2$ : —

$$2\,KNO_3 + C = 2\,KNO_2 + CO_2.$$
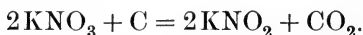
Use small quantities of the nitrate in performing this experiment.

2. **Heated** with KCN in a platinum crucible or foil, nitrates deflagrate with ignition and detonation : —

$$KNO_3 + KCN = KNO_2 + KCNO.$$
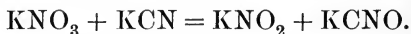
3. Mixed with copper filings and heated with concentrated $H_2SO_4$, nitrates give red fumes of $NO_2$.

4. If a concentrated solution of $FeSO_4$, free of ferric salts, be carefully added to the cold solution of a nitrate in concentrated $H_2SO_4$, so that the two solutions form distinct layers, a brown ring will be formed at their junction, $(FeSO_4)_2NO$ : —

(a) $2\,HNO_3 + 6\,FeSO_4 + 3\,H_2SO_4$
$\quad = 3\,Fe_2(SO_4)_3 + 4\,H_2O + 2\,NO$ ;
(b) $2\,FeSO_4 + NO = (FeSO_4)_2NO.$
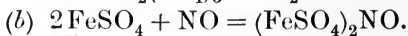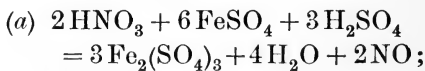
5. **Brucine** dissolved in concentrated $H_2SO_4$ gives a deep red color with nitrates. Touch the edge of the dissolved brucine with a glass rod moistened with nitrate solution; a distinct red ring will bound the rod.

6. **Reduced** with zinc dust and $H_2SO_4$, nitrates yield nitrous acid, $HNO_2$, detected by starch-KI paper.

7. **NaOH** with zinc dust and iron filings, on heating, reduces nitrates and sets $NH_3$ free :—

$$HNO_3 + 8H = NH_3 + 3H_2O.$$
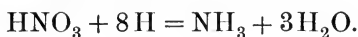
## Chloric Acid, $HClO_3$ (salt for study, potassium chlorate, $KClO_3$).

1. **Heated** on charcoal, chlorates deflagrate with vivid ignition, giving off $CO_2$ :—

$$2KClO_3 + 3C = 2KCl + 3CO_2.$$
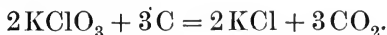
2. **Heated** with KCN in a platinum crucible, chlorates deflagrate with ignition and detonation :—

$$KClO_3 + 3KCN = KCl + 3KCNO.$$
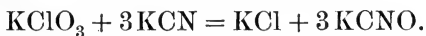
As $HClO_3$ gives up more oxygen than $HNO_3$, the chemical action in Reactions 1 and 2 is necessarily more vigorous than in those under $HNO_3$. Therefore, use very small quantities of chlorate.

3. **Concentrated** $H_2SO_4$ (a few drops), added with a pipette to a watch-glass containing a chlorate solution, liberates chlorine peroxide : —

$$3KClO_3 + 2H_2SO_4 = KClO_4 + 2ClO_2 + H_2O + 2HKSO_4.$$
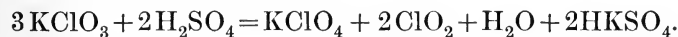
The peroxide is characterized by a disagreeable odor and a yellow coloration; also by bleaching a blue solution of indigo. Neither heat nor large quantities of reagents should be used.

4. **Brucine** behaves very much alike towards nitrates and chlorates.

## Acetic Acid, $HC_2H_3O_2$ (salt for study, sodium acetate, $NaC_2H_3O_2$).

**1. Heated** to redness, acetates are decomposed with the formation of carbonates and of acetone, $C_3H_6O$, a liquid of penetrating, pleasant, ethereal odor: —

$$2\,NaC_2H_3O_2 = Na_2CO_3 + C_3H_6O.$$

**2. FeCl₃,** a few drops, added to a *neutral* acetate solution, produces a deep red coloration, due to the formation of ferric acetate, $Fe(C_2H_3O_2)_3$. On boiling, the solution is decolorized, and brown basic ferric acetate is precipitated.

**3. Heated** with concentrated $H_2SO_4$ and alcohol, acetates yield ethyl acetate, $(C_2H_5)C_2H_3O_2$, characterized by its pungent ethereal odor: —

$$NaC_2H_3O_2 + C_2H_5OH = (C_2H_5)C_2H_3O_2 + NaOH.$$
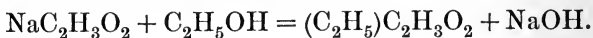
### DETECTION OF THE ACIDS OF GROUP III

Individual tests must be made for the three acids of this group, in separate portions of the original solution.

If iodides or bromides are present, they must be removed from the portion which is to be tested for $HNO_3$ by adding $HgCl_2$ solution and filtering, rejecting the precipitate. Otherwise, they would give a dark coloration on the addition of $H_2SO_4$. In testing for $HNO_3$, Reactions 3 and 4 are to be used.

In testing for $KClO_3$, Reaction 3 is to be employed. If $H_3PO_4$ is present, it is to be removed before testing for $HC_2H_3O_2$, since it forms insoluble $FePO_4$ with $FeCl_3$. (See p. 111.) Use Reaction 2 in testing for $HC_2H_3O_2$.

# CHAPTER XVI

## THE SYSTEMATIC PROCEDURE OF ANALYSIS

### PRELIMINARY TESTS

The physical properties of the substance under examination — color, odor, whether solid or liquid, etc. — are first to be noted.

**Solids.**[1] — If the substance is a solid, apply the following tests to small portions: —

(*a*) Blowpipe flame on charcoal (see Tables IV and V, pp. 48, 49).

(*b*) Heating in a closed tube (see Table II, p. 45).

(*c*) Fusion with borax bead (see Table III, p. 47).

(*d*) Flame coloration on a platinum wire (see Table VI, p. 51).

(*e*) Spectra (see Table VII, p. 58).

A larger portion of the solid is to be used for solution, in preparation for the analysis by the wet way. First, treat it with water, determining whether the whole or only a part dissolves. If it be insoluble, or only partly soluble, divide the mixture into three parts, two small and one large, which may be numbered respectively 1, 2, and 3.

To 1, in a test-tube, add some dilute HCl and boil. If still insoluble or partly insoluble, add an equal volume of concentrated HCl and boil again. If soluble, then treat 3, the largest portion, with concentrated HCl and

boil. If insoluble or partly insoluble, treat 2, first with dilute, then with concentrated $HNO_3$. If soluble, treat 3 in like manner.

If insoluble or partly insoluble in $HNO_3$ as well as in HCl and water, combine the strong HCl and $HNO_3$ mixtures, 1 and 2, and boil. If soluble, treat 3 with aqua regia. If insoluble or partly insoluble, recall which of the four solvents — water, HCl, $HNO_3$, or aqua regia — dissolved the substance most; and treat the larger portion, 3, with that solvent. Filter. Fuse the residue [1] with fusion mixture on a platinum foil or in a platinum crucible, and boil the mass with water. Sometimes this solution can be added directly to the filtrate without precipitation. Generally, however, a precipitate will be formed. In order to determine this, take small portions of both liquids and mix them. If no precipitate forms, combine the whole of both solutions. If a precipitate forms, separate analyses must be made of the two solutions.[2]

Liquids are to be tested with litmus paper to determine whether they are neutral, acid, or alkaline; and, also, small portions are to be evaporated to dryness on the water bath. No residue being left, a neutral reaction indicates that only water is present; whereas an acid or alkaline reaction indicates the presence of a volatile acid or of ammonia.

If a residue is left on evaporation : —

(*a*) A neutral reaction indicates the presence in solution of a neutral salt.

(*b*) An acid solution may be either (1) a free acid, (2) an aqueous solution of certain normal salts like

$FeCl_3$ or $CuSO_4$, which have acid reactions, (3) certain acid salts like bisulphate of potassium, $HKSO_4$, or (4) an acid solution of certain salts.

(c) An alkaline solution may contain (1) a free alkali, (2) certain normal salts like $Na_2CO_3$ which have an alkaline reaction, or (3) an alkaline solution of certain salts. In theory an aqueous solution of a basic salt should react alkaline; but as the metals which form basic salts have not a very pronounced metallic character, their alkalinity is either too weak to be detected by litmus or, being very weak, is neutralized by water.

### SYSTEMATIC ANALYSIS FOR METALS

If the solution[1] is neutral or alkaline,[2] add dilute HCl till acid; if acid, boil off the excess of acid, and when cold add dilute HCl. If a precipitate is formed, filter, and wash the residue with cold water. Analyze the residue for members of Group I, according to the directions on p. 80.

Acidify the filtrate strongly with more HCl, warm to about 70°, and pass a constant stream of $H_2S$ through it for about fifteen minutes. Then cool and dilute the solution, and, before filtering, pass $H_2S$ again till saturation is completed. If a precipitate is formed, filter, wash, and analyze for members of Group II, as directed on p. 94.

Boil off all traces of $H_2S$ from the filtrate; test for ferrous iron[3] with $K_3Fe(CN)_6$; and, if it be present, add a few drops of $HNO_3$, and boil until the iron is wholly oxidized to the ferric state. Unless the preliminary

examination has indicated conclusively whether organic matter or phosphates are absent or present, it will be necessary to test for them at this point, as is directed on p. 109. According as they are absent or present, follow the instructions given for the precipitation and separation of the members of Group III, on pp. 110 and 111.

Boil off all excess of $NH_4OH$ from the filtrate[1] which is to be examined for Groups IV, V, and VI; add $(NH_4)_2S$ in moderate excess, and if a precipitate is formed, filter and wash thoroughly. Examine it for members of Group IV according to the directions given on p. 118.

To the filtrate which may contain Groups V and VI add $NH_4Cl$, $NH_4OH$, and $(NH_4)_2CO_3$ in quantity sufficient to precipitate completely any members of Group V which may be present. Warm the mixture gently; and if a precipitate has formed, filter and wash with ammoniated water, rejecting the washings. Examine it for members of Group V, according to the directions given on p. 123.

Concentrate the filtrate which is to be examined for Group VI, and add small amounts of $(NH_4)_2SO_4$ and $(NH_4)_2C_2O_4$, to remove any traces of Ca and Ba which may be present. Filter and reject the precipitate, if one be formed; and examine the filtrate for members of Group VI, as directed on p. 127.

Concentrate some of the original solution, and test for ammonium salts with NaOH.

## SYSTEMATIC ANALYSIS FOR ACIDS

It will have been observed that the preliminary examination and the results of the analysis for metals throw much light upon the nature of the acids which may be present in the material which is being analyzed.

For example, the presence of tartaric acid may be indicated by the result of heating in a closed tube; nitrates or chlorates show their presence by deflagration, when heated on charcoal; carbonates, sulphites, sulphides, and cyanides are detected upon the addition of HCl, the reagent for the metals of Group I, by effervescence with or without characteristic odor.

Furthermore, the results of the analysis for metals will show, according as Cr and As are found absent or present, whether chromic, arsenious, and arsenic acids are absent or possibly present.

But in addition to these indications there are others, depending upon the nature of the metals present in a substance and upon the character of the solution of that substance, which may show conclusively whether certain acids or groups of acids are absent or present. If, for example, a metal of Group I is present in a neutral or acid solution, it is fair to presume that no acid of Group II can be present, since the salts of Ag, Pb, and Hg′ with such acids are almost universally insoluble, either in water or acids. If, on the other hand, a metal of Group V be found present in a neutral solution, it is presumable that no acid of Group I will be present, since the combinations between metals of Group V and acids of Group I are all practically insoluble in water.

It will be seen, therefore, that a knowledge of the solubilities which are shown in Table I, p. 34, will save much time and labor by aiding in the interpretation of the results of the analysis for metals in the manner already shown, and by diminishing the number of acids for which individual tests must be made.

In proceeding to the systematic examination for acids it is desirable to remove any heavy metals which may be present, since they are liable to obscure the reactions expected from the reagents for the acids. Accordingly, if the original substance is soluble or partly soluble, remove the heavy metals by boiling the solution with a small excess of $Na_2CO_3$ and filtering. If the substance is insoluble or partly insoluble, fuse the insoluble mass with $Na_2CO_3$ in a platinum foil or crucible, boil with water, and filter. By metathesis all the heavy metals become carbonates, and the alkali metals form soluble salts with the acids. The filtrate from either method of double decomposition can now be analyzed for acids.

Fusion decomposes $H_2C_2O_4$, $H_2C_4H_4O_6$, $HClO_3$, and $HC_2H_3O_2$; but salts of these acids are soluble in water or solvent acids, and must be sought for in the portion soluble without the aid of fusion.

Of course it is necessary to test for $H_2CO_3$ in the original substance before $Na_2CO_3$ is added.

Neutralize a small portion of the solution of the alkali salts with dilute $HNO_3$, and heat till all $CO_2$ is expelled. Add $BaCl_2$. A precipitate indicates the presence of members of Group I. Divide a larger portion of the solution into three parts, and test for

$H_2CrO_4$, $H_2SO_3$, and $H_4SiO_4$, as directed for Sub-group I, Group I, p. 138.

If any members of Sub-group I are present, add dilute HCl to another portion of the alkali salts solution, and pass $H_2S$ till the liquid smells of it. Boil off excess of HCl and $H_2S$, and divide into six parts. Examine for $H_2SO_4$, $H_3PO_4$, $H_3BO_3$, $H_2C_2O_4$, $H_2C_4H_4O_6$, and HF, as directed for Sub-group II, Group I, p. 139.

To a small portion of the alkali salts solution add a solution of $ZnSO_4$ in NaOH. If a white precipitate occurs, treat a larger portion of the solution in like manner, and filter, rejecting the white residue. Divide the filtrate, or a portion of the alkali salts solution, if $H_2S$ is absent, into three parts; and analyze for HCl, HBr, HI, HCN, $H_4Fe(CN)_6$, $H_3Fe(CN)_6$, and HCNS, as directed for Group II, p. 145.

Divide another portion of the alkali salts solution into three parts, and test for $HNO_3$, $HClO_3$, $HC_2H_3O_2$, as directed for Group III, p. 150.

# TABLE VIII — SEPARATION OF METALS

**Add HCl to the cold solution.**

- **Residue (a):** PbCl$_2$, AgCl, Hg$_2$Cl$_2$. Wash out all traces of PbCl$_2$ with boiling water.
  - **Residue (b):** AgCl, Hg$_2$Cl$_2$. Wash with warm NH$_4$OH.
    - **Residue (c):** NH$_2$Hg$_2$Cl. Dissolve in aqua regia, and confirm **Hg''** with SnCl$_2$.
    - **Filtrate (c):** 2 AgCl·3 NH$_3$. Confirm **Ag** by acidifying with HNO$_3$.
  - **Filtrate (b):** PbCl$_2$. Confirm **Pb** by adding K$_2$CrO$_4$.

- **Filtrate:** Grs. II, III, IV, V, VI. Add HCl and pass H$_2$S through the solution.
  - **Residue (a):** Sulphides of Gr. II. Wash with warm (NH$_4$)$_2$S$_x$.
    - **Residue (b):** Sulphides of Sub-group B. Boil with HNO$_3$(1:1).
      - **Residue (a'):** HgS. Dissolve in aqua regia, and confirm **Hg''** with SnCl$_2$.
      - **Filtrate (a'):** Nitrates of Pb, Bi, Cu, Cd. Add H$_2$SO$_4$.
        - **Residue (b'):** PbSO$_4$. Dissolve in NH$_4$C$_2$H$_3$O$_2$, and confirm **Pb** with K$_2$CrO$_4$.
        - **Filtrate (b'):** Nitrates of Bi, Cu, Cd. Add NH$_4$OH.
          - **Residue (c'):** BiOOH. Dissolve in a few drops of HCl, and confirm **Bi** with excess of water.
          - **Filtrate (c'):** Cu(NO$_3$)$_2$·4NH$_3$, Cd(NO$_3$)$_2$. Add KCN till blue color disappears. In a small portion confirm **Cu** with K$_4$Fe(CN)$_6$. Pass H$_2$S through the larger portion, and confirm **Cd**.
    - **Residue (c):** Sulphides of Sub-group A. Warm with conc. HCl.
      - **Residue (c):** As$_2$S$_5$. Fuse with Na$_2$CO$_3$, and confirm **As** with (NH$_4$)$_2$ MoO$_4$.
      - **Filtrate (a):** SbCl$_3$, SnCl$_2$. Add a bright iron nail. Confirm **Sn** in the liquid with HgCl$_2$. Dissolve spots on nail with H$_2$C$_4$H$_4$O$_6$, and confirm **Sb** with H$_2$S.
  - **Filtrate (b):** Grs. III, IV, V, VI
    - **Filtrate (b):** Sulpho-salts of Sub-group A. Add dilute HCl.
      - **Filtrate (c):** Reject.

## SEPARATION OF METALS (*Continued*)

Boil off all $H_2S$ from the solution (filtrate containing Grs. III, IV, V, VI).
Test for Fe' with $K_3Fe(CN)_6$, and, if present, oxidize with $HNO_3$.
Test for phosphates with $(NH_4)_2MoO_4$.
Add $NH_4Cl$ and $\underline{NH_4OH}$.

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### Residue (a): $Fe(OH)_3$, $Cr(OH)_3$, $Al(OH)_3$ or

**Method 1 — In Absence of Phosphates**
Use Method 1
Transfer residue (a) to a test-tube, and warm with $\underline{Na_2O_2}$ and water.

| Residue (b): $Fe(OH)_3$ | Filtrate (b): $Na_2CrO_4$, $Na_3AlO_3$ |
|---|---|
| Dissolve in HCl and confirm Fe''' with $K_4Fe(CN)_6$. | Add $HC_2H_3O_2$ to a portion, and confirm **Cr** with Pb $(C_2H_3O_2)_2$. Add HCl to the other portion, and confirm **Al** by adding an excess of $NH_4OH$. |

**Method 2 — In Presence of Phosphates**
Dissolve residue (a) in a little HCl, almost neutralize with $Na_2CO_3$, add $NaC_2H_3O_2$ and $HC_2H_3O_2$, and boil.

| Residue (b): $FePO_4$, $CrPO_4$, $AlPO_4$ | Filtrate (b): Phosphates of Grs. IV and V, and of Mg |
|---|---|
| Apply Method 1. | Boil, filter while hot, after having added $FeCl_3$ till colored red. |

| Residue (c): $FePO_4$, $FeO(C_2H_3O_2)$ | Filtrate (c): Chlorides of Grs. IV, V, and of Mg |
|---|---|
| Reject. | Combine with filtrate containing Grs. IV, V, VI. |

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### Filtrate: Grs. IV, V, VI. Add $NH_4Cl$ and $\underline{(NH_4)_2S}$, and boil.

| Residue (a): Sulphides of Gr. IV (see p. 160) | Filtrate: Grs. V, VI |
|---|---|
| | Dissolve in HCl (with a crystal of $KClO_3$), and boil off excess of $\overline{Cl}$. Add excess of NaOH, and boil. |

| Residue (b): $Mn(OH)_2$, $Co(OH)_2$, $Ni(OH)_2$ | Filtrate (b): $Na_2ZnO_2$ |
|---|---|
| Dissolve in a little warm HCl, nearly neutralize with $NH_4OH$, add $NH_4C_2H_3O_2$, and pass $H_2S$. | Confirm **Zn** by passing $H_2S$ through the solution. |

| Residue (c): CoS, NiS | Filtrate (c): $Mn(C_2H_3O_2)_2$ |
|---|---|
| Confirm **Co** with borax bead. Dissolve in aqua regia, almost neutralize with $Na_2CO_3$, and add KCN. Confirm **Ni** with NaBrO. | Confirm **Mn** by adding $NH_4Cl$ and $(NH_4)_2S$. |

## SEPARATION OF METALS (*Continued*)

Add (NH₄)₂CO₃ to the solution (filtrate containing Grs. V, VI).

| | |
|---|---|
| Residue (a): BaCO₃, SrCO₃, CaCO₃<br>Dissolve in HNO₃, evaporate to dryness, and digest with Ether-alcohol. | Filtrate: Gr. VI<br>Concentrate and divide into two parts:<br>First Part. — Add NH₄OH and HNa₂PO₄. A crystalline white precipitate confirms **Mg**<br>Second Part. — Expel NH₄ salts by sublimation. Test for **Na** with the flame. Dissolve in a little water and test for **K** with H₂PtCl₆.<br>Concentrate a portion of the original solution, and test for **NH₄** with NaOH. |

Residue (a) subdivides:

| Residue (b): Ba(NO₃)₂, Sr(NO₃)₂<br>Dissolve in water and add K₂CrO₄. | Filtrate (b):<br>Ca(NO₃)₂<br>Confirm **Ca**<br>by adding<br>H₂SO₄. |
|---|---|

| Residue (c):<br>BaCrO₄<br>A yellow<br>precipitate<br>confirms **Ba** | Filtrate (c): Sr(C₂H₃O₂)₂<br>Confirm **Sr** by adding NH₄OH and (NH₄)₂CO₃. |
|---|---|

## TABLE IX — ATOMIC WEIGHTS OF THE ELEMENTS
### (F. W. CLARKE)

| | H=1 | | H=1 |
|---|---|---|---|
| Aluminum . . . . . | 26.9 | Molybdenum . . . . | 95.3 |
| Antimony . . . . | 119.5 | Neodymium . . . . | 142.5 |
| Argon . . . . . | 39.6 | Nickel . . . . . . | 58.25 |
| Arsenic . . . . . | 74.45 | Nitrogen . . . . . | 13.93 |
| Barium . . . . | 136.4 | Osmium . . . . . | 189.6 |
| Bismuth . . . . | 206.5 | Oxygen . . . . . | 15.88 |
| Boron . . . . . | 10.9 | Palladium . . . . | 106.2 |
| Bromine . . . . | 79.35 | Phosphorus . . . . | 30.75 |
| Cadmium . . . . | 111.55 | Platinum . . . . . | 193.4 |
| Cæsium . . . . | 131.9 | Potassium . . . . | 38.82 |
| Calcium . . . . | 39.8 | Praseodymium . . . . | 139.4 |
| Carbon . . . . | 11.9 | Rhodium . . . . . | 102.2 |
| Cerium . . . . | 138.0 | Rubidium . . . . | 84.75 |
| Chlorine . . . . | 35.18 | Ruthenium . . . . | 100.9 |
| Chromium . . . . | 51.7 | Samarium . . . . | 149.2 |
| Cobalt . . . . | 58.55 | Scandium . . . . | 43.8 |
| Columbium . . . . | 93.0 | Selenium . . . . | 78.6 |
| Copper . . . . | 63.1 | Silicon . . . . | 28.2 |
| Erbium . . . . | 164.7 | Silver . . . . . | 107.11 |
| Fluorine . . . . | 18.9 | Sodium . . . . . | 22.88 |
| Gadolinium . . . . | 155.2 | Strontium . . . . | 86.95 |
| Gallium . . . . | 69.5 | Sulphur . . . . | 31.83 |
| Germanium . . . . | 71.9 | Tantalum . . . . | 181.5 |
| Glucinum . . . . | 9.0 | Tellurium . . . . | 126.1 |
| Gold . . . . . | 195.7 | Terbium . . . . | 158.8 |
| Helium . . . . | 3.93 | Thallium . . . . | 202.61 |
| Hydrogen . . . . | 1.0 | Thorium . . . . | 230.8 |
| Indium . . . . | 113.1 | Thulium . . . . | 169.4 |
| Iodine . . . . | 125.89 | Tin . . . . . . | 118.1 |
| Iridium . . . . | 191.7 | Titanium . . . . | 47.8 |
| Iron . . . . . | 55.5 | Tungsten . . . . | 182.6 |
| Lanthanum . . . . | 137.6 | Uranium . . . . | 237.8 |
| Lead . . . . . | 205.36 | Vanadium . . . . | 51.0 |
| Lithium . . . . | 6.97 | Ytterbium . . . . | 171.9 |
| Magnesium . . . . | 24.1 | Yttrium . . . . | 88.3 |
| Manganese . . . . | 54.6 | Zinc . . . . | 64.9 |
| Mercury . . . . | 198.50 | Zirconium . . . . | 89.7 |

## TABLE X — SOLUBILITIES [1] OF SALTS AT 18°

The *upper number* in each square gives the number of grams of the anhydrous salt held in solution by 100 c.c. of water. The *lower number* is the molar solubility, *i.e.*, the number of moles contained in one liter of the saturated solution.

| | K | Na | Li | Ag | Tl | Ba | Sr | Ca | Mg | Zn | Pb |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Cl · | 32.95 / 3.9 | 35.86 / 5.42 | 77.79 / 13.3 | $0.0_316$ / $0.0_410$ | 0.3 / 0.013 | 37.24 / 1.7 | 51.09 / 3.0 | 73.19 / 5.4 | 55.81 / 5.1 | 203.9 / 9.2 | 1.49 / 0.05 |
| Br · | 65.86 / 4.6 | 88.76 / 6.9 | 168.7 / 12.6 | $0.0_41$ / $0.0_66$ | 0.04 / $0.0_315$ | 103.6 / 2.9 | 96.52 / 3.4 | 143.3 / 5.2 | 103.1 / 4.6 | 478.2 / 9.8 | 0.598 / 0.02 |
| I · | 137.5 / 6.0 | 177.9 / 8.1 | 161.5 / 8.5 | $0.0_635$ / $0.0_71$ | 0.006 / $0.0_317$ | 201.4 / 3.8 | 169.2 / 3.9 | 200.0 / 4.8 | 148.2 / 4.1 | 419.0 / 6.9 | 0.08 / $0.0_32$ |
| F · | 92.56 / 12.4 | 4.44 / 1.06 | 0.27 / 0.11 | 195.4 / 13.5 | 72.05 / 3.0 | 0.16 / $0.0_292$ | 0.012 / 0.001 | 0.0016 / $0.0_32$ | 0.0076 / $0.0_314$ | 0.005 / $0.0_45$ | 0.07 / 0.003 |
| NO₃ · | 30.54 / 2.6 | 83.97 / 7.4 | 71.48 / 7.3 | 213.4 / 8.4 | 8.91 / 0.35 | 8.74 / 0.33 | 66.27 / 2.7 | 121.8 / 5.2 | 74.31 / 4.0 | 117.8 / 4.7 | 51.66 / 1.4 |
| ClO₃ · | 6.6 / 0.52 | 97.16 / 6.4 | 313.4 / 15.3 | 12.25 / 0.6 | 3.69 / 0.13 | 35.42 / 1.1 | 174.9 / 4.6 | 179.3 / 5.3 | 126.4 / 4.7 | 183.9 / 5.3 | 150.6 / 3.16 |
| BrO₃ · | 6.38 / 0.38 | 36.67 / 2.2 | 152.5 / 8.20 | 0.59 / 0.025 | 0.30 / 0.009 | 0.8 / 0.02 | 30.0 / 0.9 | 85.17 / 2.3 | 42.86 / 1.5 | 58.43 / 1.8 | 1.3 / 0.03 |
| IO₃ · | 7.62 / 0.35 | 8.33 / 0.4 | 80.43 / 3.84 | 0.004 / $0.0_414$ | 0.059 / $0.0_416$ | 0.05 / 0.001 | 0.25 / $0.0_257$ | 0.25 / 0.007 | 6.87 / 0.26 | 0.83 / 0.02 | 0.002 / $0.0_43$ |
| OH · | 142.9 / 18.0 | 116.4 / 21.0 | 12.04 / 5.0 | 0.01 / 0.001 | 40.04 / 1.76 | 3.7 / 0.22 | 0.77 / 0.063 | 0.17 / 0.02 | 0.001 / $0.0_32$ | $0.0_55$ / $0.0_55$ | 0.01 / $0.0_34$ |
| SO₄ · | 11.11 / $0.6_2$ | 16.83 / 1.15 | 35.64 / 2.8 | 0.55 / 0.020 | 4.74 / 0.09 | $0.0_323$ / $0.0_410$ | 0.011 / $0.0_36$ | 0.20 / 0.015 | 35.43 / 2.8 | 53.12 / 3.1 | 0.0041 / $0.0_413$ |
| CrO₄ · | 63.1 / 2.7 | 61.21 / 3.30 | 111.6 / 6.5 | 0.0025 / $0.0_415$ | 0.006 / $0.0_41$ | $0.0_338$ / $0.0_415$ | 0.12 / 0.006 | 0.4 / 0.03 | 73.0 / 4.3 | · · | $0.0_42$ / $0.0_55$ |
| C₂O₄ · | 30.27 / 1.6 | 3.34 / 0.24 | 7.22 / 0.69 | 0.0035 / $0.0_32$ | 1.48 / 0.030 | 0.0086 / $0.0_338$ | 0.0046 / $0.0_326$ | $0.0_356$ / $0.0_343$ | 0.03 / 0.0027 | $0.0_36$ / $0.0_44$ | $0.0_315$ / $0.0_55$ |
| CO₃ · | 108.0 / 5.9 | 19.39 / 1.8 | 1.3 / 0.17 | 0.003 / $0.0_41$ | 4.95 / 0.10 | 0.0023 / $0.0_411$ | 0.0011 / $0.0_47$ | 0.0013 / $0.0_413$ | 0.1 / 0.01 | 0.004 ? / $0.0_33$ ? | $0.0_41$ / $0.0_43$ |

[1] From Smith's *General Inorganic Chemistry.* Table used by permission of the author.

# NOTES

**9** 1 Two other reasons are assigned for the reaction of zinc and sulphuric acid on the dilution of the acid. Dilution increases the ionization of the acid and correspondingly increases its solvent action. Second, impurities in the zinc prevent polarization and enable the ions to discharge.

**10** 1 The term "colloid" was used by Graham to denote substances "incapable of taking crystalline form, and also distinguished by the mucilaginous character of the hydrates." The class includes glue, gums, starch, albumin, and certain arsenic and cyanogen compounds. These compounds are, for the most part, of great molecular weight. Crystalloids, on the other hand, consist of easily crystallizable substances, and include sugars, salts, and strong mineral acids and bases. — 2 *Ann. d. Chem. u. Pharm.*, **121**, 1. — 3 A porous membrane consists of unsized paper, unglazed porcelain, or parchment. It is pervious to most solvents and to crystalloid solutes, but is impervious to colloids. A semi-permeable membrane is either a colloid, or a porous membrane whose pores are filled with a colloid. Semi-permeable membranes are pervious to solvents, but impervious to both colloid and crystalloid solutes.

**11** 1 See Pfeffer, *Osmot. Untersuch.*, 1887. — 2 Not so much protoplasm itself, but rather the covering of the protoplasm.

**12** 1 *Zeit. f. phys. Chem.*, **1**, 481 (1887). — 2 Recent data by Morse and Frazer from experiments with cane sugar show that this law should be somewhat modified. *Amer. Chem. Journ.*, July, 1905. — 3 It is preferable to say that $M$ represents the gram-molecular weight and $T$ the absolute temperature.

**21** 1 A better answer to the question is that the velocity of the reaction is usually increased, and frequently the nature of the products is governed by the temperature. — 2 Inasmuch as a substance in solution is likened to a gas confined in a closed container, dilution

or increase of the volume of the solvent is equivalent to increasing the container, or decreasing the pressure.

**22** 1 Arrhenius., *Zeit. f. Chem.*, **1** (1890). — 2 The basic character also of $NH_4OH$ is lowered. In a few cases, however, — notably in that of cobalt and nickel, — the solvent action is increased. — 3 Dr. Black suggests a better explanation of this reaction : "HCl and $NaC_2H_3O_2$ are both highly dissociated, giving high concentrations of $H^+$ and $C_2H_3O_2^-$ ions ; but $H \cdot C_2H_3O_2$ is highly dissociated, or $H^+$ and $C_2H_3O_2^-$ ions cannot exist in great numbers in the same solution. Hence on mixing HCl and $NaC_2H_3O_2$, the equation $C_1 \cdot C_2 = K \cdot C_3$ for $H^+$ and $C_2H_3O_2^-$ ions must be satisfied, and as K is small, $C_3$ is large and $C_1 \cdot C_2$ small. By increasing $C_2$ representing $C_2H_3O_2^-$, $C_1$ representing $H^+$ may be still farther diminished ; or, the more $NaC_2H_3O_2$ is added, the lower the concentration of $H^+$ ions and the less the acidity of the solution."

**28** 1 Many funnels not being exactly 60° will not fit the folded filter described. To provide for angles slightly greater or smaller than 60° in folding the paper the second time to form a quadrant, the crease is made so that one half the fold shall be shorter than the other. This can be made to fit any ordinary funnel.

**45** 1 As suggested on p. 73, these tables are expressions of analysis by the dry way. They are not necessarily a guide to exact analysis, but are merely for preliminary and confirmatory observation.

**47** 1 The best way to separate the bead from the wire is to dissolve it out with hot water acidified with hydrochloric acid, and rinsed with distilled water. The loop at the end of the wire should be permanent. Frequent bending of the wire breaks it. When coloring the bead, if the quantity of the metallic salt or oxide is large enough to render it opaque, the bead can be "diluted" by taking off part of it while hot with a glass rod, and building it up again with more borax.

**54** 1 *Compt. rend.*, **55**, 576.

**56** 1 *Pogg. Ann.*, **119**, 10.

**61** 1 *Mem. II, Phil. Mag.* (4), XXII, **329**, 498. — 2 *Astronomy and Astrophysics*, **12**, 321 (1893).

**65** 1 Dr. Montgomery gives the following instructive definition of equivalent weight : "Valence is power to combine. If two amounts of the substances are equivalent they have equal power to combine or do chemical work. 'The equivalent weight of a compound is that weight which interacts with the equivalent weight of an element' (Smith). As the equivalent weight of an element is that weight which

will combine with 8 parts by weight of oxygen or with 1 part by weight of hydrogen, it follows that the equivalent of an acid, base, or salt is the molecular weight divided by the total valence of the negative, or acid, radical. If the valence of the radical is 1, the compound will interact with one equivalent of an element or compound; if the valence is 2, with two equivalents, etc.''

**68** 1 Parsons' Automatic Gas Generator, originally described by Professor Charles L. Parsons in an article entitled " Distribution of Hydrogen Sulphide to Laboratory Classes '' (*Journ. Amer. Chem. Soc.*, p. 231 (1903)), has largely solved the difficult problem of delivering hydrogen sulphide to classes, when used in connection with a distribution system easily arranged in any laboratory. This generator is sold by Eimer and Amend, New York, and is now generally used in colleges throughout the United States. The apparatus is made of stoneware, and a single generator will easily supply a class of fifty students. It is perfectly automatic in its action, and the refuse is automatically removed. The pressure on the hydrogen sulphide is almost constant, seldom varying more than two or three millimeters. Only fresh acid comes in contact with the solid reagent, and the full strength of the acid is utilized. There are no stopcocks or valves, the apparatus being controlled entirely by the exits. It is easily cleaned and refilled without taking down. It requires absolutely no attention for weeks at a time, and then only to refill the acid holder. It is always ready, and generates gas only when in use. There is no escape of gas while recharging the acid.

**77** 2 Throughout the remainder of the text all mention of reagents refers to *dilute* ones, unless otherwise designated.

**78** 1 Use an exceedingly dilute solution of ammonium hydroxide (1 : 50). At first the precipitate is white $AgOH$, changing quickly to $Ag_2O$, then to soluble $2\,AgNO_3 \cdot 3\,NH_3$.

**79** 1 $Hg_2S$ is formed at low temperature, but is broken down on warming. — 2 The precipitate has been shown to consist of metallic mercury and white $Hg'_2N \cdot NO_3$. *J. prakt. Chem.*, **39**, 204.

**80** 1 $PbI_2$ is soluble in excess of KI. Hence the precaution of adding reagents, mentioned on p. 3 (*f*), should be observed.

**81** 1 Each group precipitate should be thoroughly washed to insure the separation of that group from remnants of the filtrate, which might contain members of subsequent groups. — 2 Ice water with HCl. Lead chloride is less soluble in dilute hydrochloric acid than in water. Reject the washings. — 3 Instead of washing out the lead with hot

water on the filter, a better method is to punch a hole in the filter paper with a glass rod, wash the contents into a beaker, add water, boil about five minutes, and filter through a hot-water funnel. An ordinary funnel will usually serve the purpose. — 4 In the presence of much Hg' and a little Ag, the latter may not be found here. The residue not soluble in aqua regia should be examined for AgCl. Barnes, *Chemical News*, **51**, 97 (1885).

**82** 1 $HgI_2$ is soluble either in excess of KI or in excess of $HgCl_2$. Both re-solutions produce double salts, $Hg_2Cl_2I_2$ probably being produced by excess of $HgCl_2$.

**84** 1 This compound is probably $CuSO_4 \cdot 4 NH_3$.

**87** 1 KCNS is not a metallo-cyanide, but is conveniently classed here ; and besides, with ferric iron, it forms the so-called double salt $Fe(CNS)_3 \cdot 9 KCNS$, which is doubtless a metallo-cyanide.

**89** 1 This test should be made in a hood with a good draught to insure the removal of the poisonous arsine.

**90** 1 " Colloidal solutions occupy a place between true solutions and mechanical suspensions. The solute is present as particles which are so extremely small that they can neither be removed by sedimentation nor by ordinary filtration. By warming such solutions, and by addition of various salts, the particles may be made to increase in size until they are precipitated." Bailey and Cady's *Qualitative Analysis.*

**91** 1 $NH_4MgAsO_4$ is soluble in acids, and hence it is necessary to neutralize with $NH_4OH$.

**94** 1 Experience shows that many of the sulphides of this group are soluble in warm dilute $HNO_3$. Hence students frequently fail to precipitate completely all the sulphides of the group if $HNO_3$ is not completely removed. It is always safe to evaporate the solution to small volume to expel $HNO_3$, and then dilute with water properly acidified with HCl. — 2 The quantity of hydrochloric acid in this connection is important. This group includes eight rather widely different metals whose sulphides vary both in their solubility and in their chemical conduct towards reagents. The order of the precipitation of their sulphides from cold dilute hydrochloric acid solution is that of the metals mentioned : lead, cadmium, tin, bismuth, antimony, copper, mercury, arsenic. If, however, the quantity of the acid is increased and the solution heated to nearly boiling, the order is partly changed. The sulphides of arsenic are rendered more insoluble, while those of the other metals become more soluble. In certain quantitative determinations of arsenic its separation is effected by the use of hot

concentrated hydrochloric acid. As stated above, the arsenic sulphides are colloidal in character and, as is the habit of such compounds, are rendered more insoluble by heat and acids. The degree of acidity of the solution should be about 1 of concentrated acid to 10 of water, for the precipitation of the arsenic sulphides, and an equal volume of water added on cooling to precipitate the other sulphides. — 3 Should the solution contain nitric acid, ferric salts, chromates, and other oxidizing agents, a white precipitate of sulphur would appear here. This should not be mistaken for the sulphides of the group, all of which are colored. — 4 Dilute a portion of filtrate (a) and pass in $H_2S$ again to make sure of complete removal of Group II. The filtrate should be thoroughly tested for remnants of the group with $H_2S$. Either an excess of hydrochloric acid or an insufficiency of hydrogen sulphide might prevent the complete precipitation of the group.

**95 1** This reagent should be carefully inspected and made fresh at frequent intervals. On standing, either it is destroyed by oxidation, or it runs to the higher sulphides by the loss of ammonia. In the former case it becomes colorless, and in the latter case the yellow color changes to red. The reagent should be yellow. — 2 Though CuS is practically insoluble in $Na_2S_x$, HgS is more soluble in this reagent than in $(NH_4)_2S_x$. Hence if $Hg''$ is suspected, it is better to avoid the greater evil and use $(NH_4)_2S_x$, even though copper may be present. — 3 For detecting traces of arsenic, neither the mirror nor the ammonium molybdate test is very reliable. For this purpose, Fleitman's test, which is more delicate, is given: In a large test-tube, hydrogen is generated by heating a concentrated solution of sodium hydroxide with zinc or aluminum (Gatehouse) nearly to boiling. Introduce the arsenic solution, and above the liquid near the mouth of the tube insert a loose plug of absorbent cotton to absorb the moisture. Spread over the mouth of the tube a cup of filter paper on which is placed a crystal of silver nitrate. On warming the tube, arsine is evolved, which first forms a yellow coating on the crystal, quickly turning black. Another delicate test is Gutzeit's, which is elaborately described in the U. S. Pharmacopœia, 1900, p. 521.

**96 1** Drs. Emerson and Boggs suggest tin for zinc, and remark: "We find the precipitation of antimony by means of metallic tin is better than zinc, as it avoids the co-precipitation of tin with antimony." — 2 In this separation the zinc must not be allowed to dissolve completely, lest the tin also dissolve and oxidize before testing

with $HgCl_2$. On account of the rapid oxidation of $SnCl_2$, it should be tested quickly with $HgCl_2$, after filtering and dissolving with HCl.

**98 1** Only a small quantity of nitric acid should be used, lest some mercury be dissolved. Should this happen, the metallo-cyanide of mercury would be decomposed by hydrogen sulphide, and thus the test for cadmium would be obscured (cf. p. 86).

**99 1** Residue ($a'$) may also contain sulphur and $PbSO_4$. — **2** It is preferable to add $H_2SO_4$ before evaporating, which would drive out $HNO_3$. — **3** Lead should be entirely precipitated here, lest the remnant again appear as PbS in the test for cadmium. — **4** In filtering this mixture care should be taken to pour on the liquid slowly with a glass rod so as to collect all of the precipitate at the apex of the filter. When carefully washed, a few drops of boiling dilute hydrochloric acid are added to the residue and filtered into a beaker with about 200 c.c. of water. A solution of sodium chloride hastens the precipitation. — **5** For further confirmation of the presence of bismuth, the white precipitate is allowed to settle and is filtered. Then a solution of sodium stannite is poured on the filter. The residue turning black confirms bismuth. Noyes and Bray prescribe the following preparation of sodium stannite solution : "Add a 10 per cent solution of NaOH solution to a 10 per cent $SnCl_2$ solution until the $Sn(OH)_2$ first formed is dissolved. The solution must be freshly prepared." — **6** Another method for the detection of cadmium in the presence or absence of copper is as follows : Whether the ammoniacal solution is blue or not, add hydrochloric acid just to acid reaction, then some iron filings ; boil, and filter. Test the filtrate for cadmium by passing hydrogen sulphide gas. — **7** Should the precipitate be black, CdS would be masked by the black HgS or PbS. In this event, boil the precipitate in about 25 c.c. dilute $H_2SO_4$, add 50 c.c. water, and pass $H_2S$. A yellow precipitate confirms cadmium.

**101 1** For further discussion of this subject, see Ostwald's *Foundations of Analyt. Chem.* and Alexander Smith's *General Inorganic Chemistry.* — **2** Drs. Emerson and Boggs comment : "Boettger, following Ostwald, attributes the solubility of $Zn(OH)_2$ in $NH_4OH$ to the formation of the complex ion $Zn(NH_3)_n$ — n varying with the concentration of ammonia. The solubility of $Mn(OH)_2$ is attributed to the same cause as that of $Mg(OH)_2$, while that of the $Co(OH)_2$ and $Ni(OH)_2$ is attributed to both causes, excess of $NH_4^+$ ions especially tending to form the complex ions. The explanation of the decreased solubility of Al, Fe''', and Cr hydroxides is also a little different;

for example, when $Al(OH)_3$ dissolves in the alkalies, it gives the ion $AlO_3^-$. Water reacts with it thus : $AlO_3$ plus $3 H_2O$ give $Al(OH)_3$ plus $3 (OH)$. Therefore, any suppression of the $OH^-$ ions (as by addition of $NH_4Cl$, which is a product of the reaction) tends to cause it to go to completion, with the formation of insoluble $Al(OH)_3$." These writers then facetiously conclude: "It looks as though there are enough theories for everybody to be suited."

**103** 1 Theory of solution, p. 18. — 2 Lovén, *Zeit. f. anorgan. Chem.*, **2**, 404 (1896).

**104** 1 When ammonium hydroxide is first added in excess in the cold a pink solution is formed, but on boiling chromium hydroxide is reclaimed.

**107** 1 Single ferrous salts oxidize so quickly in the air that it is deemed expedient to use the double ammonium ferrous salt. This, however, has the disadvantage of introducing an ammonium ion which retards the precipitation by ammonium hydroxide and sodium hydroxide.

**108** 1 Krüss and Moraht give this compound as $Fe(CNS)_3 \cdot 9 KCNS$. *Ber. d. chem. Ges.*, **22**, 206. — 2 Borates and fluorides are so rarely encountered in ordinary analysis that they will not be considered here.

**110** 1 Phosphoric acid is tested for at this stage in order to determine which procedure to follow, In Absence of Phosphates or In Presence of Phosphates. — 2 The action of ammonium chloride with ammonium hydroxide on the solubility of certain hydroxides may be better understood by this additional note to the discussion of the subject, Influence of Ammonium Salts, pp. 101–104. Using more recent lettering, let $C_1$, $C_2$, $C_3$, respectively, represent $a$, $b$, $c$ in the equation $a \cdot b = c \cdot k$ (cf. p. 18). In order that any hydroxide may be precipitated, the product $C_3 \cdot K$ in the equation $C_1 \cdot C_2 = C_3 \cdot K$ must reach its maximum or so-called solubility product. In the cases of various hydroxides, averages of the solubilities of classes of them are given for comparison :

| | | |
|---|---|---|
| 1. Na, K . . . . . . . . | 20 | moles a liter |
| 2. Ba, Sr, Ca . . . . . . | 0.1 | " |
| 3. Mn, Mg . . . . . . . | 0.0002 | " |
| 4. Fe, Cr, Al, Zn, Co, Ni . . . | 0.00004 | " |

Now if an ammonium salt — say, ammonium chloride — is added to a weak ammoniacal mixture of these classes, what will happen ? Class 1 is highly ionized and very soluble ; Class 2 is less ionized and less

soluble than Class 1; Class 3 is less ionized and less soluble than Class 2; Class 4 is poorly ionized and sparingly soluble. Classes 1, 2, and 3 are all better ionized than ammonium hydroxide, and when ammonium chloride is added, by the common ion principle, the excess of $NH_4^+$ ions will suppress the $OH^-$ ions from the better dissociated hydroxides, and drive them back from the solubility product, thus preventing precipitation. In Class 4, however, the members are so poorly ionized and so insoluble in water that $NH_4^+$ ions of ammonium chloride have no opportunity to suppress the $OH^-$ ions of the hydroxides. The results are that ammonium chloride in the presence of slight excess of ammonium hydroxide redissolves manganese and magnesium hydroxides, but does not affect those of ferric iron, chromium, aluminum, zinc, cobalt, and nickel. All of these conditions obtain only when the excess of ammonium hydroxide is slight. When a large excess of ammonium hydroxide is used, the conditions and results are different from those just discussed. Ferric hydroxide is practically unaffected, but all the other metallic hydroxides considered are more or less redissolved. The re-solution of aluminum hydroxide is caused by its amphoteric or dual nature. It is both a weak acid and a weak base, and dissociates into two systems of ions. As an acid it loses water and dissociates into $H^+$ and the aluminate anion $AlO_2^-$; as a base it dissociates into the aluminum cation $Al^+$ and $3\,OH^-$. Now when ammonium hydroxide is added, its $OH^-$ ions unite with the $H^+$ ions to form water. But the system $C_H \cdot C_{AlO_2}$ is constant, and the suppression of its $H^+$ ions causes more $Al(OH)_3$ to be dissociated into $H^+$ and $AlO_2^-$ until, if sufficient ammonium hydroxide is added, the whole of the $Al(OH)_3$ runs into $H^+$ and $AlO_2^-$. During the progress of these changes the free $NH_4^+$ ions unite with $AlO_2^-$ ions to form $C_{NH_4} \cdot C_{AlO_2}$ of high solubility product. Should a better ionized base — say, sodium hydroxide — be used, solution will be effected more quickly and with less of the reagent. As regards chromium, zinc, manganese, cobalt, nickel, and magnesium, an excess of ammonium hydroxide unites with them to form complex metalloammonia cations, thus requiring more molecules of the hydroxides of the simple cations to reach concentration. The effect, of course, is to redissolve these hydroxides in varying degrees, nickel being affected most and chromium least. The addition of ammonium chloride to an ammonium hydroxide solution of the hydroxides in question weakens the ionization of the ammonium hydroxide by suppressing the $OH^-$ ions. This prevents the re-solution of aluminum hydroxide.

On the other hand, the increase in the number of $NH_4^+$ ions increases the number of metallo-ammonia ions of the other metals, and thus prevents their precipitation. — 3 Barium carbonate is added to insure a complete separation of the iron group from manganese. In the presence of ammonium salts, ammonium hydroxide does not precipitate manganese hydroxide, but the tendency of the latter is to oxidize quickly to an insoluble basic oxide, which frequently precipitates it out of due course. Barium carbonate forms with the members of the iron group insoluble basic carbonates, but produces no precipitate from neutral or slightly acid solutions of manganese salts. — 4 Filtrate (*b*) contains barium which was added as a reagent, and, of course, it will be found in Group V. But a test for its presence was made before adding $BaCO_3$. Phosphates of barium, strontium, calcium and magnesium are insoluble in alkalies, but are soluble in acids. Hence if these salts are present, they are precipitated by $NH_4OH$ and redissolved by HCl. For this reason filtrate (*b*) should be combined with filtrate (*a*).

**114** 1 Unless care is taken to perform the experiment in the *cold*, the compound $ZnSO_4 \cdot 4\,NH_3$ will be formed instead of $(NH_4)_2ZnO_2$. — 2 Green and more stable manganous sulphide may be formed by boiling the pink variety with an excess of the reagents, ammonium sulphide and ammonium hydroxide.

**118** 1 This washing should be done with warm water containing a little $(NH_4)_2S$. The appearance of manganese in the filtrate is due to oxidation or the formation of a colloidal precipitate on account of having no "salt" in the wash water. Also, we find that the NiS may appear in the filtrate where $(NH_4)_2S$ is used as a precipitant. This may be precipitated by boiling with acetic acid. — 2 If the NaOH is not added in considerable excess, the $Zn(OH)_2$ will reprecipitate on boiling. Hence, according to Fresenius it is best not to boil, but to stir with cold NaOH solution.

**119** 1 In case manganese is not found in residue (*a*), this brown precipitate is to be examined for manganese. After filtering, if the brown color persists, it is probably nickel sulphide, which can be precipitated by boiling with acetic acid. — 2 Possibly a better way of confirming manganese is to evaporate the solution to dryness and fuse with dry $Na_2CO_3$ and $KNO_3$ to quiet fusion on a platinum foil. A green mass on cooling confirms manganese.

**120** 1 A large excess of KCN should be avoided, as the excess must be neutralized with NaBrO. On the other hand, a small excess

must be added both to precipitate cobaltous cyanide and to redissolve it as a double cyanide.

**126** 1 $NH_4OH$ only partly precipitates $Mg(OH)_2$. — 2 Sodium cobaltic nitrite, $Na_3Co(NO_2)_6$, may be substituted for $H_2PtCl_6$ in testing for ammonium and potassium compounds. In this event, substitute acetic acid for alcohol.

**133** 1 For complete descriptions of this method, see Fresenius' *Quantitative Chem. Analysis*, 16th ed., p. 117, and Crookes' *Select Methods in Chem. Analysis*, p. 26.

**146** 1 Edward Hart gives the following excellent method for testing chlorides, bromides, and iodides in presence of each other : The iodide is oxidized with ferric sulphate and the iodine distilled off and tested with starch paper ; the bromide is then oxidized with potassium permanganate, and the bromine removed and tested by distilling in chloroform ; and the liquid is finally tested for the chloride with silver nitrate. *Amer. Chem. Journ.*, **6**, 346.

**151** 1 Professor Shingler adds this instructive supplement to preliminary tests for solids : " If the substance is a solid, apply the following tests : (1) If it is a paint or pigment, extract for several hours with ordinary ether, and use residue for subsequent tests. (2) If it contains arsenic or other volatile constituents, add concentrated sulphuric acid to decompose and nitric acid repeatedly to oxidize, heating over a small flame. Continue until the liquid is clear and colorless. Then evaporate until fumes of $SO_3$ appear. Dilute, filter, and proceed as usual. (3) If it contains aluminum or is largely mineral matter, as a baking powder, add concentrated nitric acid and heat at first gently and then more strongly. Repeat the operation several times until carbonaceous matter is consumed. Then add hydrochloric acid and boil. Proceed as usual."

**152** 1 Noyes and Bray prefer to treat the residue with concentrated sulphuric acid and hydrofluoric acid in lieu of alkali carbonates. In some respects this has its advantages, but the method requires the frequent use of expensive platinum crucibles by inexperienced students; and also in the presence of barium (and to some extent strontium and lead) difficultly soluble sulphates are formed. *Journ. Amer. Chem. Soc.*, **29**, 140. — 2 In the event the two solutions produce a precipitate or the fusion does not effect solution, the aqueous extract or mixture from the crucible is evaporated to dryness. The mass is then taken up with boiling water and filtered. The filtrate contains the chlorides of sodium and potassium, and those of barium and

strontium may be present. The filtrate can be tested directly for barium and strontium (cf. p. 124). The residue may be silica and the chlorides of silver and lead. Boil with ammonium acetate and some dilute acetic acid. Filter and wash thoroughly with hot water. Test filtrate for lead with potassium chromate. Warm residue with potassium cyanide solution. Filter, and test filtrate for silver by adding excess of nitric acid. (*This must be done in a hood to avoid breathing the deadly prussic acid.*) Transfer the residue to a platinum crucible, and test for silica by adding solution of hydrofluoric acid and a few drops of sulphuric acid.

**153** 1 In order to guard against accidents and as a reserve for tests for ammonium, a portion of this original solution should be set aside for future examination. — 2 If the solution is alkaline, it may contain various solutes, namely, silver salts, sulpho-salts, silicic acid, metallic hydroxides, etc. In this condition the solution should be acidified with nitric acid, and if a precipitate forms, more acid should be added and the solution warmed. If the precipitate does not redissolve, the mixture is filtered and the residue examined as other substances insoluble in water. The filtrate is evaporated to expel nitric acid, diluted with water, and examined as other acid or neutral solutions. — 3 No matter what the valence of iron was originally, at this stage of the analysis it must necessarily be bivalent or *ous*. See reactions, bottom of p. 107.

**154** 1 If, on standing, a brown precipitate is formed, filter, and test residue for manganese ; if the filtrate remains brown, boil with acetic acid, filter, and test residue for nickel. Use filtrate for Group IV.

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